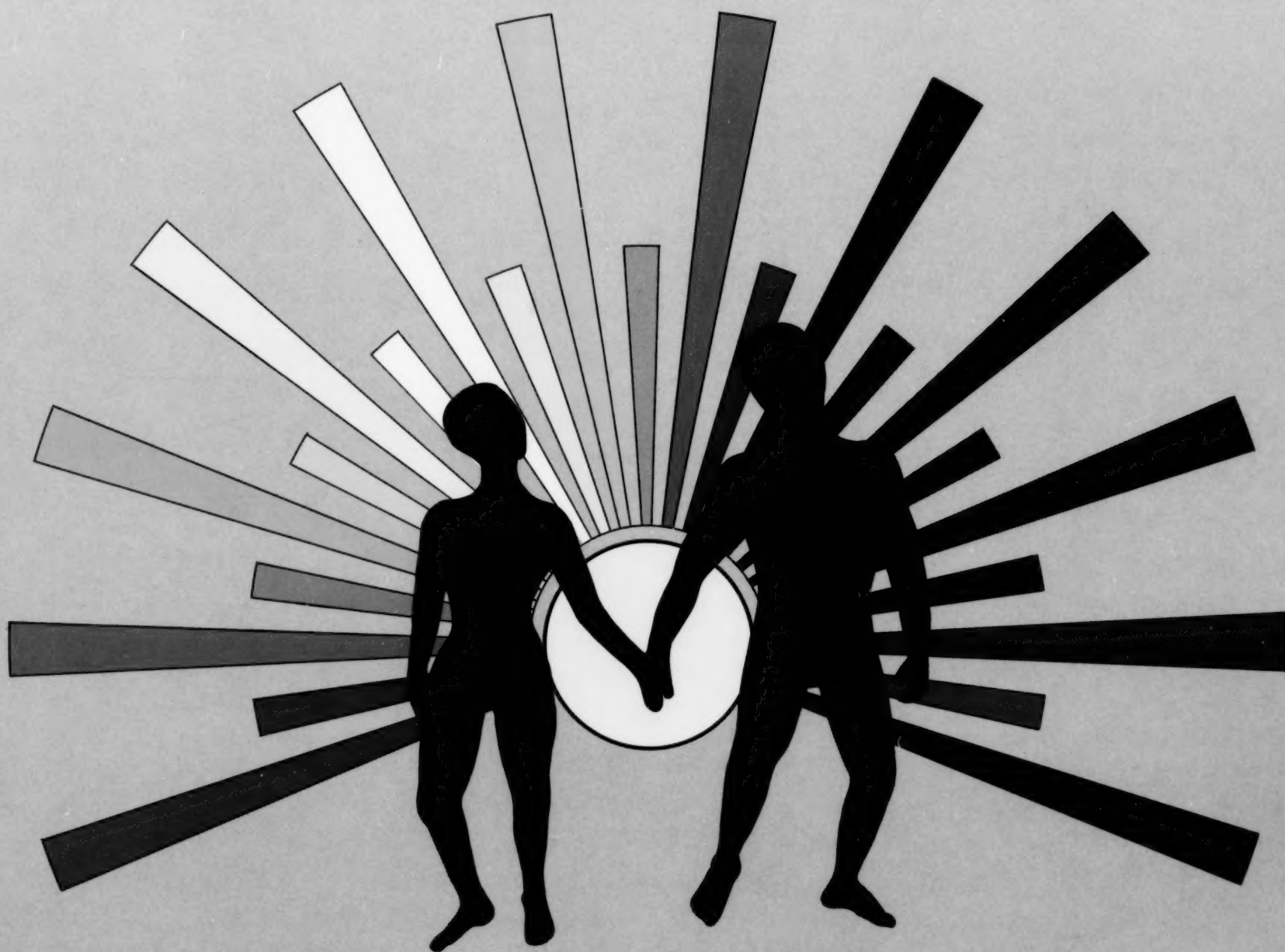

the Science of the Total Environment

**An International Journal for Scientific Research
into the Environment and its Relationship with Man**



**SPECIAL ISSUE:
PATHWAYS OF MAN-MADE SO₂, NO_x
AND METALS IN THE ENVIRONMENT**
Edited by L. Pawłowski and H.M. Seip

the Science of the Total Environment

An International Journal for Scientific Research into the
Environment and its Relationship with Man

Managing Editor

E. I. Hamilton (*Tavistock*)

Associate Editor

J. O. Nriagu (*Burlington*)

Editorial Board

F. Adams (*Antwerp*)
B. J. Alloway (*London*)
A. W. Andren (*Madison, WI*)
M. Benarie (*Brétigny-sur-Orge*)
J. P. Boon (*Den Burg*)
D. Brune (*Oslo*)
W. Burkart (*Villigen PSI*)
P. J. Craig (*Leicester*)
J. Fergusson (*Christchurch*)
L. Fishbein (*Washington, DC*)
J. R. Goldsmith (*Beer-Sheva*)
R. S. Hamilton (*Enfield*)
M. Harada (*Kumamoto*)
R. M. Harrison (*Colchester*)
A. V. Holden (*Pitlochry*)
K. J. Irgolic (*Graz*)
G. V. Iyengar (*Gaithersburg, MD*)

R. Kiyoura (*Tokyo*)
Z. Konrad (*Zagreb*)
H. A. M. de Kruijf (*Bilthoven*)
A. Lafontaine (*Brussels*)
J. N. Lester (*London*)
D. A. Lord (*Port Elizabeth*)
R. J. Norstrom (*Ottawa, Ont.*)
M. C. O'Riordan (*Chilton, Didcot*)
L. Pawłowski (*Lublin*)
R. J. Pentreath (*Lowestoft*)
O. Preining (*Vienna*)
E. Sabbioni (*Ispra*)
M. Stupfel (*Le Vésinet*)
G. Topping (*Aberdeen*)
P. Valenta (*Jülich*)
J. I. Waddington (*Copenhagen*)

Scope

The journal is primarily an international medium for the publication of research into those changes in the environment caused by man's activities. Specifically, it is concerned with the changes in the natural level and distribution of chemical elements and compounds which may affect the well-being of the living world, and ultimately harm man himself. Emphasis is given to applied environmental chemistry. The subjects covered include: (a) application of techniques and methods of chemistry and biochemistry to environmental problems; (b) pollution of the air, water, soil and various aspects of human nutrition; (c) environmental medicine, when the effect of abnormalities in the level and distribution of chemical elements and compounds are given prominence; (d) the use of interdisciplinary methods in studies of the environment; (e) environmental planning and policy.

Subscription

The Science of the Total Environment is published in 36 issues per year and has twelve volumes (87-98) in 1990. The subscription price is Dfl. 2400.00 plus Dfl. 336.00 (postage) = Dfl. 2736.00 total price. Please send your order to: Elsevier Science Publishers B.V., Journals Department, P.O. Box 211, 1000 AE Amsterdam, The Netherlands. Telephone: (020) 5803 911. Telex: 18582 ESPA NL.

Our p.p.h. (postage, packing and handling) charge includes surface delivery of all issues, except to subscribers in Argentina, Australia, Brazil, Canada, Hong Kong, India, Israel, Malaysia, Mexico, New Zealand, Pakistan, P.R. China, Singapore, South Africa, South Korea, Taiwan, Thailand and the U.S.A., who receive all issues by air delivery (S.A.L. - Surface Air Lifted) at no extra cost. For the rest of the world, airmail and S.A.L. charges are available upon request.

Claims for missing issues will be honoured, free of charge, within three months after publication date of the issues.

Customers in the U.S.A. and Canada wishing information on this and other Elsevier journals, please contact Journal Information Center, Elsevier Science Publishing Co. Inc., 655 Avenue of the Americas, New York, NY 10010. Telephone: (212) 633 3750.

All back volumes are available at Dfl. 190.00 plus Dfl. 27.00 (p.p.h) = Dfl. 217.00 per volume.



UNIVERSITY OF CALIFORNIA, IRVINE

POSITION ADVERTISEMENT ENVIRONMENTAL HEALTH

The Program in Social Ecology at the University of California, Irvine is recruiting for an assistant professor, tenure track position in the area of Environmental Health Science and Policy.

Applicants should have received a Ph.D. in environmental sciences, environmental chemistry, molecular and environmental biotechnology or biochemistry.

The successful candidate should have demonstrated experience in laboratory or field research related to environmental sciences or health. Ability to team statistics and environmental testing methodology is desirable.

The program in Social Ecology grants B.A., M.A., and Ph.D., degrees. The 30 full-time faculty have multidisciplinary interests and expertise in environmental sciences, public health, demography, urban planning, environmental law, and environmental psychology.

The Social Ecology Building houses four laboratories: ultraclean monitoring, water quality, microbial ecology and bioremediation laboratory, radiocarbon dating and environmental chemistry laboratory, and a full-scale environmental simulation laboratory.

Candidates should submit a letter of application, curriculum vitae and names of 3 references to:

*Closing data for
applications is
November 30, 1990.
The University of
California is an Equal
Opportunity/Affirmative
Action Employer.*

Dr. Betty H. Olson, Chair
Environmental Health Search Committee
Program in Social Ecology
University of California
Irvine, CA 92717

WATER TREATMENT

JOURNAL OF THE DESALINATION AND WATER RE-USE SOCIETY, CHINA

Edited by Shi Song (Hangzhou, China)

International Advisory Board:

G. Alberti (*Perugia, Italy*)
M. Balaban (*Ed. Desalination*)
D. Barba (*Rome, Italy*)
K.W. Böddiker (*Geesthacht, FRG*)
R.C. Clayton (*London, UK*)
T. Davis (*Union, NJ, USA*)
E. Drioli (*Naples, Italy*)
A.G. Fane (*Kensington, NSW, Australia*)
S.-T. Hwang (*Cincinnati, OH, USA*)
S.E. Jørgensen (*Copenhagen, Denmark*)
T. Matsuura (*Ottawa, Canada*)
M. Nakagaki (*Kyoto, Japan*)
W. Pusch (*Frankfurt, FRG*)
B.R. Smith (*Clayton, Vic., Australia*)
H. Strathmann (*Tübingen, FRG*)
L.K. Wang (*New York, NY, USA*)

Supported by a
Chinese Editorial Board

Water Treatment specializes in the field of water desalination and re-use. It contains scientific papers, research reports, and reviews on all kinds of applied techniques of water treatment, including special topics such as membrane separation, desalination, and other treatment techniques using physical chemistry and biochemistry methods. The journal aims to serve all those who are engaged in water treatment. It welcomes original research papers and state-of-the-art reviews on all fields of water treatment. It is hoped that these contributions and discussions on any new concept or practice will help to promote the development of the profession not only in China but throughout the world.

Abstracted/Indexed in:

Chemical Abstracts, Chemical Eng. Abstracts, Theoretical Chemical Eng. Abstracts

Subscription Information:

1990: Vol. 5 (4 issues)
US\$ 284.00 / Dfl. 568.00 incl. postage
ISSN 0921-2639

For a free sample copy of the journal, write to:

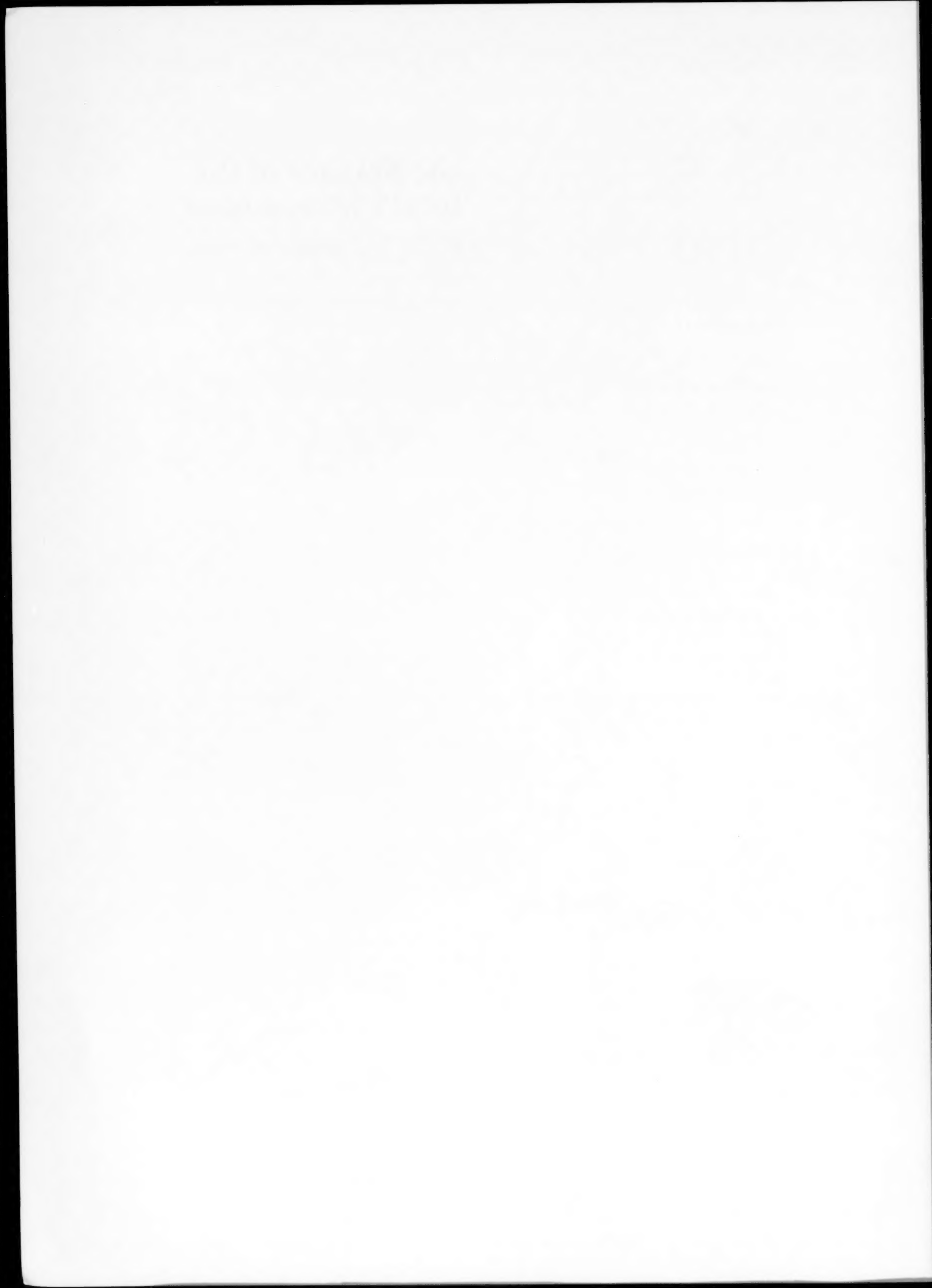


ELSEVIER SCIENCE PUBLISHERS

P.O. Box 211, 1000 AE Amsterdam, The Netherlands
P.O. Box 882, Madison Square Station, New York, NY 10159, USA

the Science of the Total Environment

volume 96 (1990)



the Science of the Total Environment

An International Journal for Scientific Research into the
Environment and its Relationship with Man

MANAGING EDITOR

E. I. Hamilton (*Tavistock*)

ASSOCIATE EDITOR

J. O. Nriagu (*Burlington*)

EDITORIAL BOARD

- | | |
|---|--|
| F. Adams (<i>Antwerp</i>) | R. Kiyoura (<i>Tokyo</i>) |
| B. J. Alloway (<i>London</i>) | Z. Konrad (<i>Zagreb</i>) |
| A. W. Andren (<i>Madison, WI</i>) | H. A. M. de Kruijf (<i>Bilthoven</i>) |
| M. Benarie (<i>Brétigny-sur-Orge</i>) | A. Lafontaine (<i>Brussels</i>) |
| J. P. Boon (<i>Den Burg</i>) | J. N. Lester (<i>London</i>) |
| D. Brune (<i>Oslo</i>) | D. A. Lord (<i>Port Elizabeth</i>) |
| W. Burkart (<i>Villigen PSI</i>) | R. J. Norstrom (<i>Ottawa, Ont.</i>) |
| P. J. Craig (<i>Leicester</i>) | M. C. O'Riordan (<i>Chilton, Didcot</i>) |
| J. Fergusson (<i>Christchurch</i>) | L. Pawłowski (<i>Lublin</i>) |
| L. Fishbein (<i>Washington, DC</i>) | R. J. Pentreath (<i>Lowestoft</i>) |
| J. R. Goldsmith (<i>Beer-Sheva</i>) | O. Preining (<i>Vienna</i>) |
| R. S. Hamilton (<i>Enfield</i>) | E. Sabbioni (<i>Ispra</i>) |
| M. Harada (<i>Kumamoto</i>) | M. Stupfel (<i>Le Vésinet</i>) |
| R. M. Harrison (<i>Colchester</i>) | G. Topping (<i>Aberdeen</i>) |
| A. V. Holden (<i>Pitlochry</i>) | P. Valenta (<i>Jülich</i>) |
| K. J. Irgolic (<i>Graz</i>) | J. I. Waddington (<i>Copenhagen</i>) |
| G. V. Iyengar (<i>Gaithersburg, MD</i>) | |

Volume 96 1990



ELSEVIER

AMSTERDAM—OXFORD—NEW YORK—TOKYO

Articles are abstracted/indexed in:

Biological Abstracts
Chemical Abstracts
Current Contents/Agriculture, Biology & Environmental Sciences
Environmental Periodicals Bibliography
Excerpta Medica
Focus On: Global Change
Geo Abstracts
Oceanographic Literature Review
PASCAL/CNRS
Selected Water Resources Abstracts

© 1990, ELSEVIER SCIENCE PUBLISHERS B.V.

0048-9697/90/\$03.50

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior written permission of the publisher, Elsevier Science Publishers B.V., P.O. Box 330, 1000 AH Amsterdam, The Netherlands.

Upon acceptance of an article by the journal, the author(s) will be asked to transfer copyright of the article to the publisher. The transfer will ensure the widest possible dissemination of information.

Submission of an article for publication entails the author(s) irrevocable and exclusive authorization of the publisher to collect any sums or considerations for copying or reproduction payable by third parties (as mentioned in article 17 paragraph 2 of the Dutch Copyright Act of 1912 and in the Royal Decree of June 20, 1974 (S. 351) pursuant to article 16b of the Dutch Copyright Act of 1912) and/or to act in or out of Court in connection therewith.

Special regulations for readers in the U.S.A. - This journal has been registered with the Copyright Clearance Center, Inc. Consent is given for copying of articles for personal or internal use, or for the personal use of specific clients. This consent is given on the condition that the copier pay through the Center the per-copy fee for copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Law. The per-copy fee is stated in the code-line at the bottom of the first page of each article. The appropriate fee, together with a copy of the first page of the article, should be forwarded to the Copyright Clearance Center, Inc., 27 Congress Street, Salem, MA 01970, U.S.A. If no code-line appears, broad consent to copy has not been given and permission to copy must be obtained directly from the author(s). All articles published prior to 1980 may be copied for a per-copy fee of US\$2.25, also payable through the Center. This consent does not extend to other kinds of copying, such as for general distribution, resale, advertising and promotion purposes, or for creating new collective works. Special written permission must be obtained from the publisher for such copying.

No responsibility is assumed by the Publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the materials herein. Because of rapid advances in the medical sciences, the Publisher recommends that independent verification of diagnoses and drug dosages should be made.

Although all advertising material is expected to conform to ethical (medical) standards, inclusion in this publication does not constitute a guarantee or endorsement of the quality or value of such product or of the claims made of it by its manufacturer.

This issue is printed on acid-free paper.

PRINTED IN THE NETHERLANDS

SPECIAL ISSUE

**PATHWAYS OF MAN-MADE SO₂, NO_x
AND METALS IN THE ENVIRONMENT**

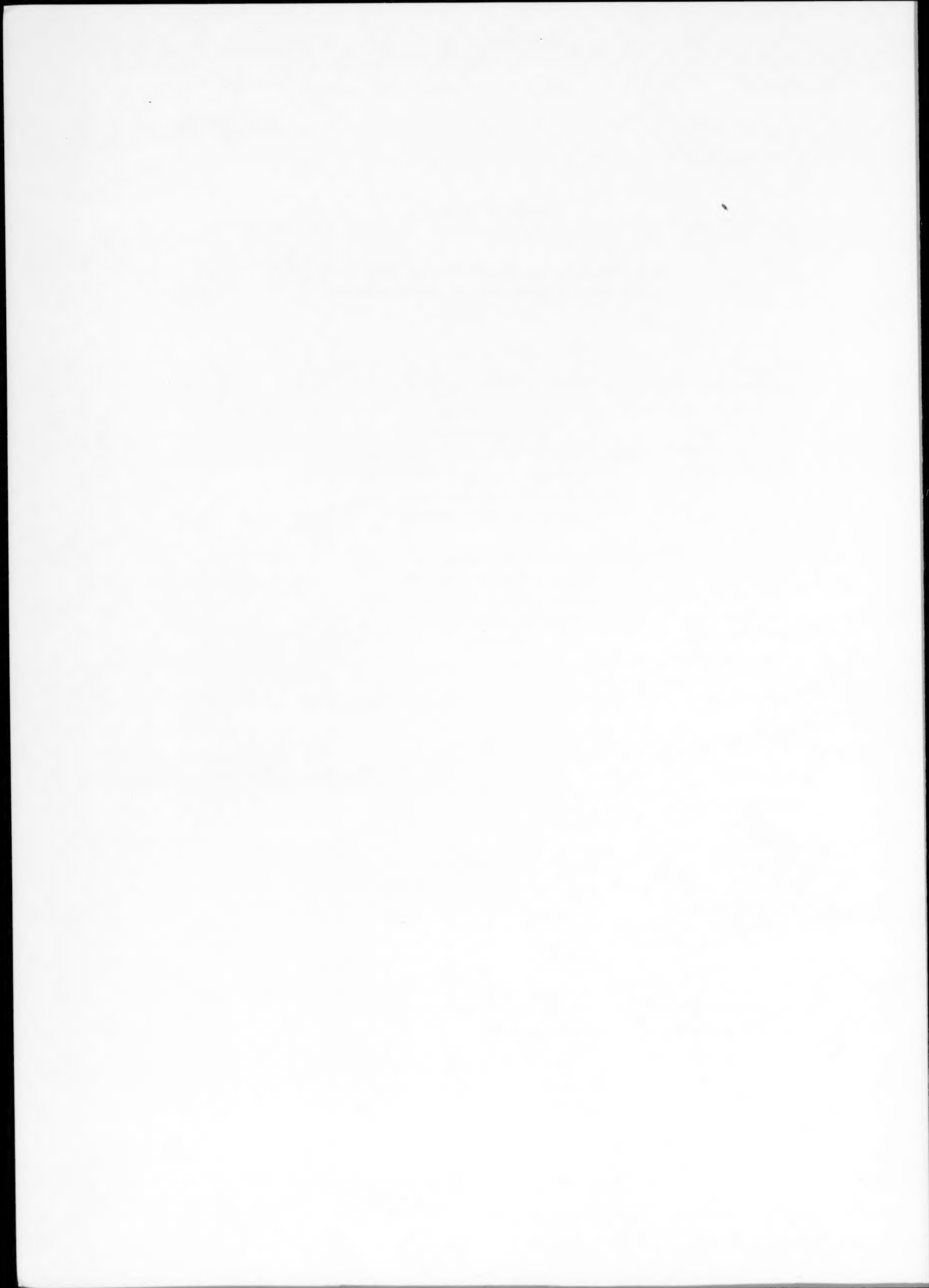
Edited by

L. Pawłowski

*Department of Water and Wastewater
Technology, Technical University
of Lublin, 40 Nadbystrzycka Str.,
20-618 Lublin, Poland*

H.M. Seip

*Department of Chemistry,
University of Oslo, P.O. Box 1033,
Blindern 0315, Oslo 3,
Norway*



CONTENTS

<i>Special Issue: Pathways of Man-made SO₂, NO_x and Metals in the Environment</i>	vii
<i>Preface</i>	ix
Chemical threat to the environment in Poland	
L. Pawłowski (Lublin, Poland)	1
Acid precipitation monitoring and research. Review of current Norwegian activities	
G. Taugbøl (Oslo, Norway)	23
Acidification in Norway — loss of fish populations and The 1000-Lake Survey 1986	
B.O. Rosseland and A. Henriksen (Oslo, Norway)	45
Acid precipitation: Biological monitoring of streams and lakes	
A. Fjellheim and G.G. Raddum (Bergen, Norway)	57
Concentrations of atmospheric SO ₂ , NO ₂ and dust in the Lublin coal basin area	
Z. Kozak, A. Figurski, J. Niećko, D. Kozak and R. Gierżatowicz (Lublin, Poland)	67
Calculations of long-range transported sulphur and nitrogen over Europe	
T. Iversen (Oslo, Norway)	87
The role of nitrogen oxides in the long-range transport of photochemical oxidants (Abstract only)	
Ø. Hov (Lillestrøm, Norway)	101
Metal solubility and pathways in acidified forest ecosystems of South Sweden	
D. Berggren, B. Bergkvist, U. Falkengren-Grerup, L. Folkeson and G. Tyler (Lund, Sweden)	103
Occurrence of heavy metals in water, phytoplankton and zooplankton of a mesotrophic lake in eastern Poland	
S. Radwan, W. Kowalik and C. Kowalczyk (Lublin, Poland)	115
Accumulation of heavy metals in a lake ecosystem	
S. Radwan, W. Kowalik and R. Kornijów (Lublin, Poland)	121
Total and extractable heavy metal content of some soils of the Lublin Coal Mining Region	
T. Filipek and L. Pawłowski (Lublin, Poland)	131
Assessment of aluminium mobilization and pathways in the Birkenes catchment, southern Norway	
R. Vogt, H.M. Seip, N. Christophersen and S. Andersen (Oslo, Norway)	139
Are mathematical models useful for understanding water acidification?	
A. Stone and H.M. Seip (Oslo, Norway)	159

Aluminium mobilization in soil and stream waters at three Norwegian catchments with different acid deposition and site characteristics N. Christophersen (Oslo, Norway), C. Neal (Wallingford, U.K.), R. Vogt (Nesoya, Norway), J.M. Esser (Ås, Norway) and S. Andersen (Oslo, Norway)	175
Effect of nitrogen on drought resistance of Norway spruce and Scots pine P. Nilsen (Ås, Norway)	189
Lead and cadmium contamination of soil and vegetables in the Upper Silesia region of Poland J. Gzyl (Katowice, Poland)	199

Preface

The articles in this issue are based on presentations at a meeting held in Jabłonna (near Warsaw) in October 1988: Pathways of Man-made SO_2 , NO_x , and Metals in the Environment. The participants came from Poland and Scandinavia (mostly Norway). An important goal of the meeting was to contribute to an increased cooperation between Poland and Norway on environmental problems. Early in 1989, Poland and Norway signed an agreement to cooperate in this area.

We have also decided to include an extract of a report of the Polish Chemical Society: 'Chemical Threat to the Environment in Poland' [1]. This report gives a broad view of the environmental situation in Poland. Most of the issues were discussed at the meeting.

As in most cases, our cooperation was initiated by a personal meeting which in our case took place during a meeting of the Presidium of the Working Party of Chemistry and the Environment formed under the auspices of the Federation of European Chemical Societies. Through mutual scientific visits we were able to obtain first hand information about similarities in, and differences between, the environmental problems in Poland and Norway. As an illustration, we show in Fig. 1 the pH of precipitation and SO_2 concentrations in air over Europe for 1985. It should be noted that while the SO_2 concentration in air is much higher in Poland than in Norway, the acidity of the precipitation is as high in southernmost Norway (4.2 – 4.3) as it is in Poland due to neutralization by dust in the latter area. In general, Poland is one of the most polluted countries of Europe, and the degradation of the environment is considerably more advanced in Poland than in Norway. Forest damage occurs over large areas and metal concentrations in soils and plants are high; surface waters are polluted both by organic material and by metals (see paper by Pawłowski, pp. 1–21). In comparison, most of Norway is fairly clean. However, some of the fjords are quite heavily polluted and the air in some areas is not of satisfactory quality. The most serious problem in Scandinavia, however, is acidification of water and soils. Large areas are highly vulnerable to acidification due to weathering-resistant rocks and shallow soils.

In spite of the differences in environmental problems of the two countries, there are strong reasons for cooperation. One reason is that pollutants do not stop at national borders. Thus Poland is one of the larger contributors to sulphur deposition in Norway, but, on the other hand, receives about 50% of its sulphur from abroad, mostly from Czechoslovakia and the DDR. More important is the scientific inspiration that may result from such cooperation. There are some basic requirements for environmental research. It is not sufficient just to register pollution levels, it is necessary to understand processes and mechanisms. The pathways of the various pollutants in the environment must be understood in order to take the most effective counter-

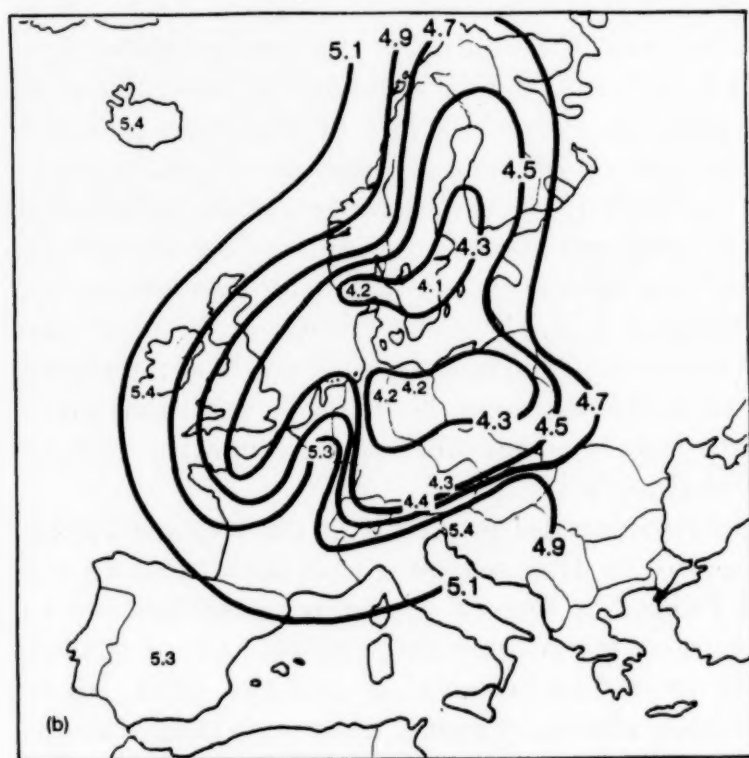
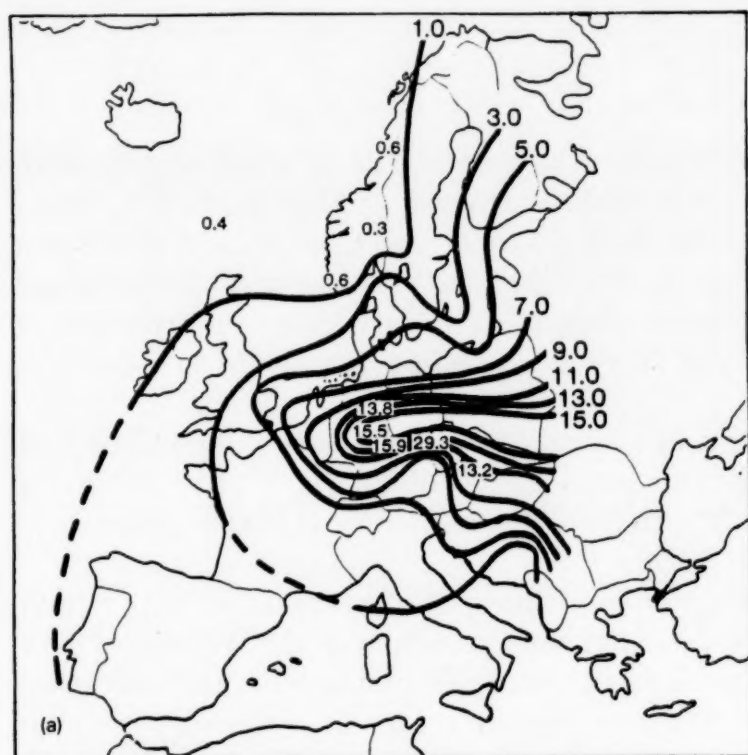


Fig. 1. Annual mean concentrations (μgSm^{-3}) of SO_2 in air (a), and annual mean pH (b) of precipitation in Europe in 1985. From the Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe (EMEP) [3].

measures. In some areas our knowledge of basic mechanisms is limited. It is therefore not appropriate to concentrate only on applied research; if basic research is neglected, serious and costly errors may result. Mathematical modelling is a useful tool for testing hypotheses about chemical behaviour and for making predictions about the fate of chemicals. Models may also be used to systematize large amounts of data and to design field studies by clarifying the type of observations needed to solve the problem at hand. Several aspects of modelling were discussed at the workshop.

It is encouraging that the governments of both countries take environmental problems seriously. The Norwegian government has a special responsibility since the present prime minister chaired 'The World Commission on Environment and Development' established by the United Nations [2]. In Poland the newly elected government is making a serious effort to solve environmental problems.

The workshop was held in an informal atmosphere with ample time for open discussions. We are grateful to all the participants for their active cooperation. Alex Stone (Department of Chemistry, University of Oslo) has greatly assisted in improving the style of most of the articles. We would also like to express our appreciation to Dr Eric Hamilton, Managing Editor of *The Science of the Total Environment*, for the opportunity to publish material from our workshop and for his help in editing this issue.

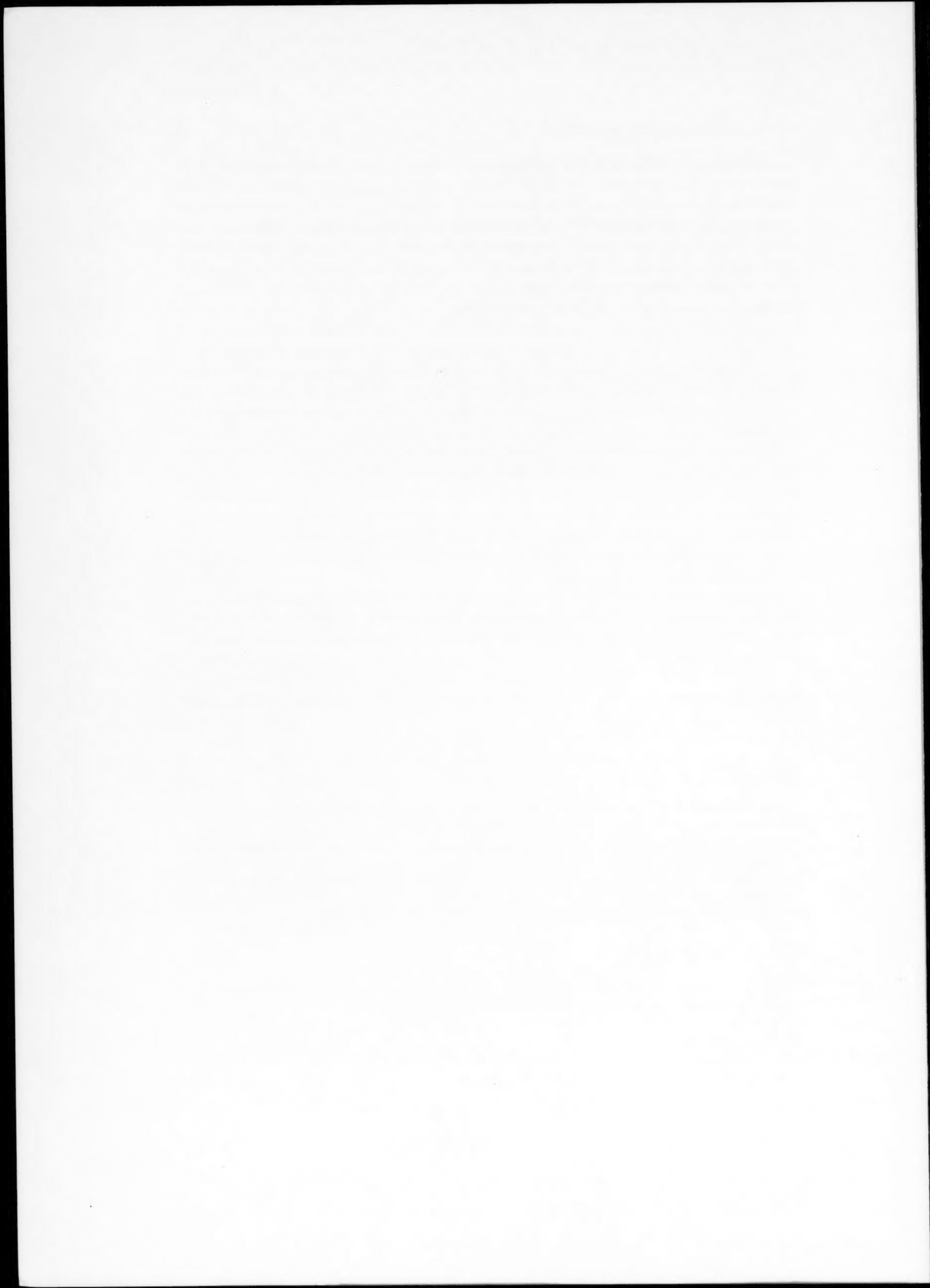
Finally, we thankfully acknowledge support from the Norwegian Ministry of the Environment, the Polish Central Research Project CPBP No. 04.10, and a fellowship to L. Pawłowski from the Norwegian Council for Scientific and Industrial Research.

HANS M. SEIP
Oslo, Norway

LUCJAN PAWŁOWSKI
Lublin, Poland

REFERENCES

1. L. Pawłowski and Z. Kozak (Eds), Chemical Threat to the Environment in Poland. Report of the Environmental Protection Section of the Polish Chemical Society, 1988.
2. Our Common Future, The World Commission on Environment and Development, Oxford University Press, Oxford, 1987.
3. J. Schaug, J.E. Hanssen, K. Nodop, B. Ottar and J.M. Pacyna, Summary Report from the Chemical Co-ordinating Centre for the Third Phase of EMEP. EMEP-CCC-Report 3/87, Norwegian Institute for Air Research, Box 64, 2001 Lillistrom, Norway.



CHEMICAL THREAT TO THE ENVIRONMENT IN POLAND*

LUCJAN PAWŁOWSKI

Department of Water and Wastewater Technology, Technical University of Lublin, 20-618 Lublin (Poland)

ABSTRACT

Pollution of the environment in Poland is described and the concentrations of SO₂, NO_x, dust and metals in air are characterized. Surface water is classified according to sanitary standards, and the concentrations of heavy metals in the River Vistula are presented. Soil is mainly polluted with heavy metals; appropriate data depicting the situation are given. Characteristics of food product contamination are also presented.

INTRODUCTION

The industrial and ecological transformations which took place in various regions of Poland after World War II have led to a psychosocial problem arising from the contamination of many areas on a scale which is biologically irreversible. An extensive policy of industrialization of the country which ignored ecological and psychosocial factors, led not only to senseless destruction of a considerable area of Poland, but also created situations of prolonged stress for about one-third of the Polish population living in areas of so-called ecological crisis.

Studies performed by scientists of the Catholic University of Lublin on psychological reactions in situations of ecological crisis indicate that changes observed in the environment are seen as highly feared threats by inhabitants of regions exposed to harmful industrial pollution. These studies clearly indicate that inhabitants of ecologically endangered regions experience progressive deprivation of many needs. Degradation of the natural environment does not only threaten the biological existence of man, it is also an important factor in psychological degradation of the inhabitants of the towns and countryside subjected to harmful products from industrial development. The breaking of ecological barriers leads, consequently, to the breaking of barriers of psychological resistance in people who are forced to live and work in

* This paper is based on the Polish Chemical Society Report "Chemiczne Zagrożenia Środowiska w Polsce" (Chemical Threat to the Environment in Poland), published by the Technical University of Lublin in 1988. The report was written by a team of specialists: J. Barcicki, A. Biela, Cz. Dabrowski, E. Garścia, M. Gromiec, H. Jurkowska, A. Kabata-Pendias, P. Kyć, S. Kozłowski, A.L. Kowal, J. Kurbiel, H. Mazur, M. Piotrowska, I. Pollo, M. Roman, S.A. Rybicki, J. Szczypa and S. Tyszkiewicz, and chaired by L. Pawłowski and Z. Kozak.

conditions of increasingly visible accumulation of industrial pollutants. This is particularly evident for people living in the most ecologically endangered regions, where a particularly high incidence of psychosomatic diseases, neurological disorders and negative changes in self-esteem were observed. The data demonstrate a close relation between the observed negative changes in the natural environment and self-esteem, which is an important component of an individual's personality. Environmental protection is, therefore, essential for the maintenance of the physical and mental health of a human population.

In 1983, the Environmental Protection Division of the Polish Chemical Society initiated the preparation of several short reports on the "Chemical Threat to the Environment in Poland" which provided information about the gravity of the situation. In addition, various sectors of the economy were mobilized to provide more effective financial support for the protection of the environment.

The first report [1], published in 1984, resulted in a number of discussions and fulfilled its original purpose, although it was also the subject of strong criticism from the Government.

In 1986, the second conference on the theme "Chemical Threat to the Environment in Poland" was organized with the intention of preparing a second report. The conference took place in Lublin on 15-18 October 1986. The data presented in this publication are based on that conference and on the final, second report with the same title [2].

CHEMICAL CONTAMINATION OF AIR

It is difficult to obtain reliable numerical data concerning the concentrations of various air pollutants actually found in Poland. The monitoring of air covers only 10% of the area of the country, and the analyses are usually performed periodically, in normal working hours, so that the results may not always correctly reflect the actual state of the atmosphere.

The magnitudes of emissions of the four main air contaminants, dust, CO, SO₂ and NO_x, can be found in the GUS* publications.

CAUSES AND SOURCES OF AIR CONTAMINATION

Contamination of the air in Poland has geographical, technological and political causes. The main cause of air pollution appears to be the method of industrialization adopted in Poland after World War II. The development of heavy industry, and the exploitation and processing of raw materials were emphasized. Material and energy consuming technologies were given high priority. Protection of the environment was neglected. For many years, environmental pollution was not even recognized as a problem.

The geographical causes are associated with a large influx of contaminants

* GUS, the Main Statistical Office of Poland.

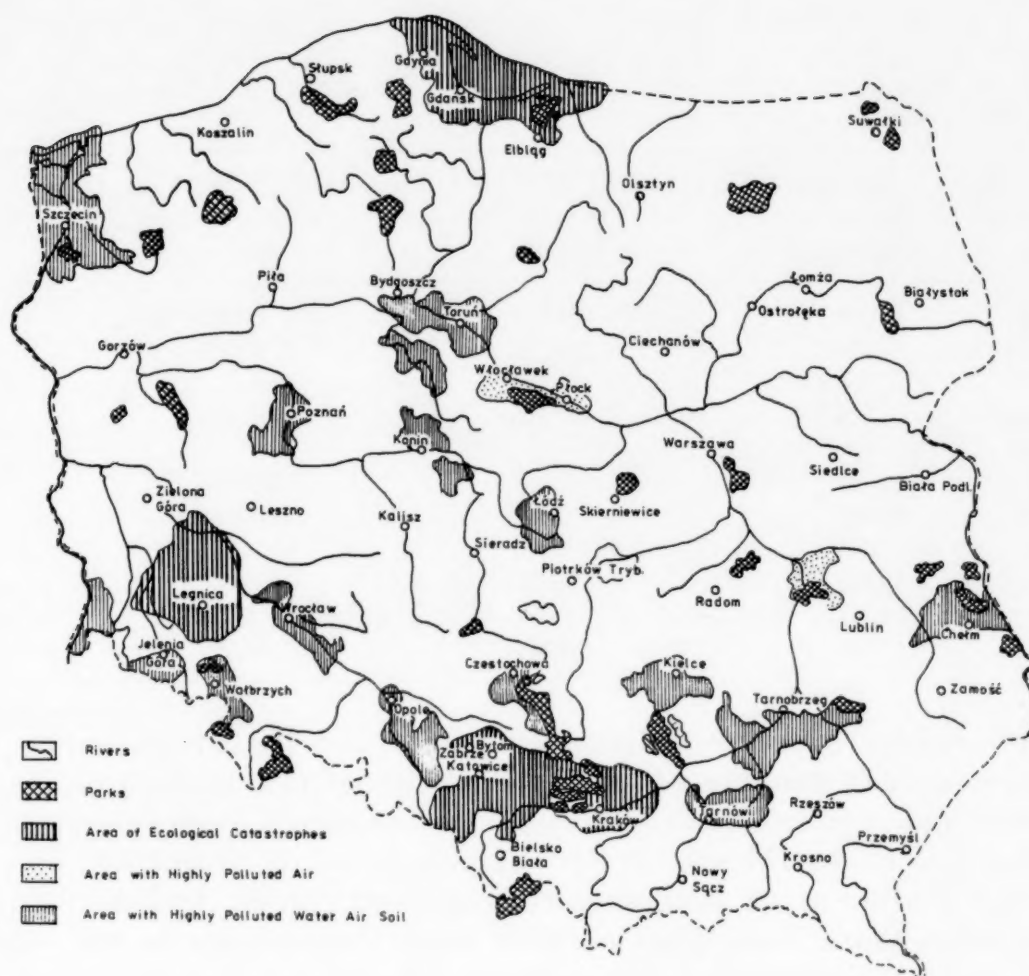


Fig. 1. Map of Poland with highly polluted areas indicated.

from neighboring countries; ~50% of the sulfur deposition in Poland originates in other countries, mostly in the DDR and Czechoslovakia.

In Poland emphasis has been placed on short-sighted economic advantages arising from concentrating both the extraction of raw materials and their

TABLE 1

Sources and emissions of the four main air contaminants during 1984/85 (Poland)

Sector of economy	Emission ($\times 10^6$ t year ⁻¹)			
	Dust	SO ₂	NO _x	CO
Power stations	1.2	1.94	0.40	0.02
Industry	1.4-1.7	1.26	0.64	1.2-1.5
Transport		0.10	0.35	0.8-1.2
Residential accommodation	0.4-0.6	1.00	0.11	0.8-1.6
Total	3.3-3.5	4.30	1.50	2.8-3.7

TABLE 2

Emissions from the 10 most harmful industrial plants, 1986 (GUS publication "Environmental Protection and Water Management" Warsaw, 1987, pp. 184-185)

Plant	Emission (t year ⁻¹)		
	Dusts	Gases	SO ₂
Lenin steelworks	61088	484636	26985
Katowice steelworks	54354	257522	34087
Głogów I copper smelter	1776	183175	62112
Power stations			
Turów	94666	230202	215804
Belchatów	23943	233558	190181
Jaworzno III	12459	176115	161313
Połaniec	13237	175647	165961
Siersza	26988	149608	108306
Łaziska	15181	147267	95783

conversion into finished products at the same location. This led to a concentration of emission sources, sometimes to such a degree that the local capabilities for atmospheric and environmental self-cleaning have clearly been exceeded. This occurred mostly in Silesia, in the neighborhood of Turoszow and Belchatów, and in other areas, such as in the region of Pulawy. In 1985, 83% of the air contaminants came from only 94 production plants (~80% in 1986), confirming the fact that emission sources are concentrated in a small area.

More than 84% of the total gaseous contaminants and 77% of the dust are emitted in areas of ecological crisis, covering, in total, 10.3% of the surface area of Poland. In Poland, 27 areas are defined as approaching ecological catastrophe.

Emission data for four main air contaminants are given in Table 1; Table 2 lists nine industrial plants, out of the list of 94 main emitters of air contaminants, with amounts of the main four contaminants emitted by each.

Low stacks are responsible to a large extent for high concentrations of contaminants near ground level. The maximum deposition of dust, 1504 t km⁻² year⁻¹, was recorded at Zabrze-Biskupiec (Silesia).

A comparison of actual current data with data from the earlier report shows a slight reduction in the emission of contaminants only in the sector of power generation, whereas in all other sectors there was an increase in emissions.

Evaluation of the state of atmospheric contamination in Poland on the basis of emissions of the four main contaminants (SO₂, NO_x, CO and dust) only, would be a drastic oversimplification and would neglect some very important factors. Much information concerning local air contamination problems can be found in reports prepared for the individual districts. In the report for the Head of Katowice district, for example, the deposition of dust is often as much as six

TABLE 3

The number of chemicals and the number of times that the maximum allowable air concentrations were exceeded in Silesia in 1983 [4]

City	Number of chemicals exceeding the maximum allowable concentration	Total number of times the maximum allowable concentrations were exceeded (average per year)
Zabrze	24	250
Bytom	24	170
Chorzów	21	165
Gliwice	21	165
Katowice	18	150
Knurów	18	110
Rybnik	16	90
Piekary Sl.	15	95
Będzin	15	87
Czeladź	15	91
Sosnowiec	15	89
Tarnowskie Góry	14	97
Trzebinia	14	70
Jaworzno	13	69
Zawiercie	13	58
Racibórz	12	48
Ogrodzieniec	12	48
Olkusz	11	42
Pilica	11	42
Wolbrom	9	31
Klucze	9	34

times greater than the maximum allowable level*, the concentration of suspended dust 7–35 times, the concentration of SO_2 1–2 times, the concentration of NO_x 1.3–6 times, and the concentration of CO as great as 21 times the allowable level. The concentration of benzo[a]pyrene is often 3–62 times higher than the allowable level, and lead 1.5–196 times.

The most serious situation was recorded in Zabrze and Bytom where the maximum allowable concentration was exceeded by 24 substances (54 were monitored) and, in Zabrze, the maximum allowable concentration is exceeded, on average, 250 times per year (see Table 3).

In addition to the sources discussed so far, three sources of contamination require special attention. These are exhaust from internal combustion engines, tobacco smoke and emissions from residential areas.

The average annual deposition of sulfur (as S) is 7.73 t km^{-2} in Poland, 7.63 in the DDR, 8.5 in Czechoslovakia, 5.6 in the FGR and only 2.7 in France.

The exhaust from internal combustion engines with spark ignition is a very

* Standards for allowable levels are usually the same as recommended by WHO.

strong source of lead, estimated at $> 8 \text{ kg year}^{-1}$ for each kilometer of paved road in Poland.

The exhaust from internal combustion engines with self-ignition is, on the other hand, a source of relatively large amounts of nitrogen oxides, which in areas of intense automobile traffic, coupled with long periods of sunny weather, often leads to photochemical smog.

The exhaust from either type of engine, particularly if not well tuned, is also a source of products of incomplete fuel combustion. The products from incomplete combustion and nitrogen oxides in the atmosphere undergo photochemical oxidation reactions, forming very toxic products with peroxide and/or ozone. Even though the number of cars in Poland is less than in many other countries, pollution from this source is significant.

Tobacco smoking, without doubt, is very harmful. Smoking is a matter of individual choice; prohibition of tobacco growing would be ineffective. However, smokers ($\sim 70\%$ of the Polish population) should not be allowed to endanger other people who inhale tobacco smoke, by a process called passive smoking, in smoke-filled rooms. Tobacco smoke, as shown in pharmacological studies, contains about 4000 chemical compounds with distinctly harmful effects on the lungs, blood and the body as a whole, including carcinogenic effects, particularly in the lungs and the upper respiratory system.

The increase in the cases of lung cancer in Poland is clearly correlated with an increase in cigarette smoking. The frequency of lung cancer in Poland in the fifties placed the country 22nd in Europe. Now it is in sixth place and, if the observed rate of growth is maintained, Poland may well occupy first place in the world in the nineties.

By comparing recent observations with the previous reports, a distinct improvement as regards passive smoking can be seen. Prohibition of smoking at railway stations, on trains and in confined places has been introduced.

It appears that this type of solution could be used to limit other contaminant emissions to the atmosphere without a large monetary investment. One could, for example, limit contamination from automobile exhaust by issuing, via road militia, tickets ordering the tuning of engines, under threat of punishing owners of polluting cars.

The problem of chemical emission from building materials is not yet fully understood. An example of this type of emission is the toxic paint used in some schools and living quarters in Gdansk contrary to building code requirements and in disregard of alarming findings from regional sanitary and epidemiological stations.

Air contaminants found within buildings include formaldehyde volatilized from furniture, chlorophenols and other components from xylamite, benzene and other aromatic hydrocarbons vaporized from various paints, and vinyl chloride from PVC (the nonpolymerized fraction). The list of such substances is very long.

Air contamination of homes is particularly dangerous and undesirable since, in addition to effects on healthy adults, such pollution can have a large

impact on already frail or vulnerable individuals such as children, the sick and the old.

EFFECTS OF AIR CONTAMINATION

Human life takes place at the bottom of an ocean of air formed by the atmosphere on the Earth's surface. Hence, air contaminants contribute directly or indirectly to the disturbance of metabolic processes, and can contribute to increased vulnerability to sickness, increased mortality and thus shorter life expectancy.

Diseases of the respiratory system develop largely because of air contamination. The number of cases of tumors in the period 1960–1980 increased five-fold, and the main disease among them was lung cancer. About 100 000 inhabitants of Poland die prematurely each year as a result of "nicotinism" (nicotine poisoning) due to both active and passive smoking.

The threshold concentration of SO_2 , above which coniferous forests suffer damage, is estimated to be $20 \mu\text{g SO}_2 \text{ m}^{-3}$, which corresponds to a deposition of $\sim 7.5 \text{ t SO}_2 \text{ km}^{-2}$. Coniferous trees in Poland are therefore exposed to the action of SO_2 in concentrations exceeding the threshold and, therefore, the forests suffer serious damage.

Conifer needles are more exposed to the action of SO_2 than are broad leaves since they remain on the trees for several years, whereas broad leaves stay for only one spring–summer season. Healthy coniferous trees may have as many as seven sets of needles of different ages present at the same time, whereas it is found that trees exposed to contamination have less. The number depends on the degree of damage, and, in heavily polluted areas, trees may have only one set.

Forests are also destroyed even more by ozone and the very reaction OH radical than by SO_2 .

The threshold of harmfulness of SO_2 to human health is estimated to be $60 \mu\text{g m}^{-3}$ as an annual average, which corresponds to a deposition of $\sim 20 \text{ t SO}_2 \text{ km}^{-2}$.

Reduction in the grain harvest occurs when concentrations of SO_2 exceed $80 \mu\text{g m}^{-3}$ as a yearly average. In Poland, average annual SO_2 concentrations exceeding $20 \mu\text{g m}^{-3}$ are observed in a number of areas. In Upper Silesia, there are local regions where the average annual concentration of SO_2 has reached $300 \mu\text{g m}^{-3}$. High concentrations of SO_2 are also found in Silesia, Cracow, the Gdansk area, Poznan and many other localities. In areas with large cities, the average annual concentrations of SO_2 exceed $350 \mu\text{g m}^{-3}$.

It is anticipated that, in 1991, there will be stricter regulations concerning the allowable concentration of SO_2 , and that the highest allowable average yearly SO_2 concentration will be set at $21 \mu\text{g m}^{-3}$.

If the emission of SO_2 continues to increase at the present rate, and no new methods of desulfurization of gaseous emissions are introduced, one can predict that the allowable concentrations of SO_2 will be exceeded over an area $> 50\%$ of the country.

A number of air contaminants that appear together with SO_2 may act synergistically and may increase the harmful effects of SO_2 on flora, fauna and buildings. Nitrogen oxides and SO_2 in the atmosphere undergo oxidation, and with water, form nitric and sulfuric acid, respectively. These acids are washed from the air by precipitation and form acid rain, the pH of which may sometimes be < 3 . Rain of this kind, percolating through the soil down to the roots of trees, becomes more concentrated and more acidic, mobilizing toxic metals in the soils, of which soluble aluminum salts are particularly harmful to the root system.

The action of acid rain is especially harmful in mountainous regions where the sparse soil cover is unable to buffer the acids contained in the rain water. The forest covering Izerskie Góry (Southwest Poland) is almost completely destroyed.

CHEMICAL CONTAMINATION OF WATER

In Poland, the purity of various waters is estimated by analyzing 49 parameters, but in a routine control of quality only a limited number of indicators are determined.

It is obvious that the final result depends on the number of parameters considered and the frequency of water sampling. The classification is made by appropriate departments in national or local administrations. It consists of assigning particular sections of streams to define classes of purity, according to the present and planned use of water from these sections.

Water assigned to Class I would be suitable for supplying populations with potable water and for breeding fish such as salmon. Waters of Class II would be suitable for breeding other types of fish, and for consumption by domestic animals; they could also be used for bathing. Waters of Class III would be suitable for industrial purposes (with the exception of processes which require water of high quality, i.e. potable water) and for irrigation of agricultural land and orchards.

The National Inspection of Environmental Quality examined, in total, 21 375 km of river (50% of total length of Polish rivers), and established that: 1083 km or 5.1% are of Class I; 4406 km or 20.8% are of Class II; 5518 km or 25.8% are of Class III. Hence, 11 007 km or 51.7% fall within the classification range. The remaining 48.3% (10 368 km) contained water which did not fulfil the conditions for any class. In addition, 2883 villages and small towns experience a constant shortage of water, and 3861 others suffer periodic water shortage (up to 3 months per year). These data are alarming. It is understandable, therefore, why the Polish Church has organized a foundation which strives to supply villages with water of satisfactory quality.

CAUSES AND SOURCES OF WATER CONTAMINATION

It is very difficult to describe in detail the contamination of natural water systems by wastewaters because of their highly variable chemical composition.

TABLE 4

Evaluation of water supply sources in 1980 and 1986 [3]

	1980	1986
Pipelines		
Satisfying the quality requirement	44.1%	25%
Not satisfying the quality requirement	55.9%	75%
Bathing facilities		
Satisfying the quality requirement	72.9%	84.6%
Not satisfying the quality requirement	37.1%	25.4%

In the period 1980–1986, the amount of wastewater requiring purification did not change significantly. The amount of wastewater purified biologically increased by 32%. This fact should be considered as a positive feature.

Water purity can also be described indirectly by data from the sanitary evaluation of water pipeline systems and bathing facilities supplied from surface waters. Such data are presented in Table 4, and they indicate that sanitary conditions of water pipeline systems deteriorated during the period 1980–1986, but some improvement was noted for bathing facilities during the same period.

A particularly disturbing situation appeared in the upper parts of the Rivers Vistula (Wisła) and Odra. The upper Vistula, and its tributaries in the area of Silesia, showed an increase in contamination, mainly in the form of increased concentrations of minerals primarily from mine waters containing high concentrations of salt. However, it is not only Silesian mines that are responsible for the increased contamination of the Vistula. A considerable increase in the COD, and the concentrations of nitrogen compounds and heavy metals, indicates an increased contaminant load of domestic, industrial and agricultural origin.

Each day the mines dump into the Vistula and Odra basins 650 000 m³ of water containing > 6300 t of chlorides and other contaminants. As the coal is mined from deeper and deeper layers, the salinity of the mine waters increases.

Mercury may serve as an example of the high level of metallic microcontaminants in the River Vistula. The concentration of mercury in all sporadically performed analyses exceeds 0.015 mg dm⁻³, whereas the maximum allowable value for Class II purity is 0.005 mg dm⁻³. Concentrations of other toxic, and no less dangerous, heavy metals also exceed the permissible value, for example lead (0.1 mg dm⁻³), which has reached 0.25 mg dm⁻³. Hence, the threat to the Vistula comes not only from coal mining, but also from other branches of industry which dump toxic, biogenic and organic wastes.

Apart from the Vistula, deterioration in the last decade has also affected the

quality of rivers which should be of Class I purity on account of their use as sources of drinking water. This group contains, among others, foothill tributaries of the Vistula, such as the Sola, Raba, Dunajec, Wisloka, San and Wislok. In the River Dunajec, formally classified as Class I purity, bacterial contamination (as determined by faecal *E. coli*) causes degradation of this river to purity Class III. In the River San, above Dynowa, a site fairly remote from sources of contamination, the quality of the water from a sanitary viewpoint does not even correspond to Class III purity. The characteristic value of the *E. coli* titre was 0.001 (instead of 1.0), and the number of bacteria (determined in gelatin at 20°C) reached 600 000 colonies. The increased contamination of the Upper Vistula affects the water quality in its lower reaches and presents a threat to community and industrial supply and to anticipated agricultural irrigation.

In general, from an assessment of the quality of flowing surface waters one can establish that it continues to be bad and is not improving. There is a great discrepancy between the actual and the required purity; there are only 5% of river sections of Class I purity, and nearly 50% of the river sections are contaminated above any allowable limits.

In addition to the bad quality of flowing water, one can also observe a serious threat to lakes. Occasional tests indicate that the majority of lakes inspected are contaminated and that in about half of them some irreversible degradation processes have started.

Shallow underground waters are becoming contaminated to greater and greater degrees. The reasons for this contamination lie in the chemical agents applied in agriculture (chemical fertilizers and plant protection agents), sewage dumped on the ground in areas without sewage systems, waste and garbage dumps, and litter from industrial and residential areas, as well as contaminants from the atmosphere. An indication of the degree of contamination can be obtained from data from the sanitary evaluation of well water, presented in Table 5.

The data show that, among public and domestic wells, the percentage of examined wells in which water is acceptable from a sanitary standpoint is < 37.1%.

Poor quality limits the direct utilization of water in industry, decreasing the

TABLE 5

Sanitary evaluation of well water [3]

Public well	Water grade (percentage of controlled wells)					
	1980			1986		
	Good	Uncertain	Bad	Good	Uncertain	Bad
Towns	29.4	25.3	45.3	29.9	18.7	51.4
Villages	26.8	22.0	51.2	37.1	10.7	52.2

production efficiency of manufacturing plants, causing faster deterioration of production equipment, and resulting in a lowering of the quality of final products. Poor natural water quality also necessitates using complicated and expensive treatment methods. Contamination also creates potential threats to human health. One of the main reasons for water contamination is the lack of, or poor condition of, wastewater treatment plants. Another factor is the improper use of existing facilities, so that the expected cleansing effects are not realized.

During one year, 1 ha of land may absorb 30–50 t of manure. One large domestic animal (the cow) produces yearly ~10 t of manure. On average, in Poland, there are 1.5 large domestic animals per hectare. The conditions exist, therefore, for full absorption of manure without harm to the environment. However, an excessive concentration of animals on farms in some areas creates problems related to the disposal of manure.

In Poland, of 45 000 villages, only about 10 000 have a piped water supply, and this is not always linked to a sewage system. With the lack of toilets flushing faecal matter with water, the waste is dumped directly onto the soil. It then undergoes decomposition and conversion to substances assimilated by plants. In general, therefore, in such villages there is no accumulation of faecal matter to a degree which may cause poisoning of the soil or water. As the rural localities gradually become equipped with flushing toilets, faecal matter will be mixed with other wastes and the load of contaminants reaching groundwaters will become larger.

Of the 10 000 villages that have a piped water supply, only a few tens of villages have sewage pipes. Even fewer of these villages possess sewage treatment plants.

Studies by the Institute of Rural Medicine in Lublin have shown that 75–86% of wells is contaminated with disease-causing bacteria, especially from the *Salmonella* group. In many cases, even if water from a rural well is tolerable with respect to chemical contaminants, it may be prohibitively contaminated with harmful bacteria.

The shortage and poor quality of potable and sanitary water cause deterioration of the state of the health of the population and, in extreme cases, lead to the outbreak of epidemics.

WATER RESOURCES IN POLAND AND THEIR DEFICIT

Man is consuming large amounts of water in three branches of the economy: in industry, in agriculture, and for municipal purposes. The average yearly outflow of rivers in Poland is 58.6 km³ and in dry years it falls to 34 km³. If we neglect heated water from cooling systems, this amount of water would be sufficient to dilute about 4.0 km³ of wastewater to the level at which self-purification could occur. However, the yearly amount of wastewater in Poland is more than three times this volume.

Therefore, Poland is not rich in water. The measure of availability of water

resources is the amount of water corresponding to one inhabitant in a defined unit of time. In Poland, this amount is half the average value for the whole of Europe, and 10 times smaller than for the U.S.S.R. or the U.S.A. In this respect Poland may be compared to a desert country such as Egypt. Shortage of water limits the development of industry and agriculture.

The planned intensification of agriculture up to the year 2000 will require 4–8 km³ water yearly. Similar amounts of water will be required by power stations, even if one assumes that recycling will be used. The water demand of a nuclear power plant is 1.5–2 times larger than the demand of a conventional plant. Hopefully, Poland will stop building nuclear power stations. A conventional power plant with a closed cycle generating 600 MW uses as much water as a city with a population of half a million. The shortage of water calls into question the realization of planned undertakings in industry and agriculture.

CHEMICAL CONTAMINATION OF SOIL

Excessive amounts of various chemicals, particularly trace elements, disturb the complex processes occurring in soils. They disadvantageously affect the circulation of elements naturally present in the soil, they limit or excessively increase the assimilation of elements by plants and they accelerate the transport of elements to water bodies.

At present, chemical contamination of soils is mainly a result of human activities, leading to the degradation of soils.

In contrast to air and water pollution, contaminated soils cannot be easily purified and the process of self-purification via the circulation of elements throughout the lithosphere is very slow, requiring thousands of years.

"The future of nations depends on their food" proclaimed Brilla-Savarin, and a soil expert, Voisina, added "and on soil which produces this food". According to Voisina, soil and manure shape the fate of man and animals. In this context, the plea SOS — Save Our Soils! popularized in Poland, and in the whole world by people who realize the problem, becomes understandable. chemically degraded soils show disadvantageous changes in biological activity and physical properties and become more vulnerable to erosion, both by water and air.

Chemical degradation of soils is caused primarily by two processes:

- processes leading to a change in soil acidity or alkalinity;
- processes leading to accumulation in soils of trace elements, particularly metals.

The consequences of these two processes will be discussed later.

CAUSES AND SOURCES OF SOIL CONTAMINATION

A significant part of Poland is affected by processes which devastate or chemically degrade the soil. Although there is still a lack of accurate data on contamination of arable land by trace elements, it is known that there is a real

TABLE 6

Annual emissions of arsenic, cadmium and lead by some European countries (1979 data) [5]

Country	Total emission (t year ⁻¹)			Relative emission (g ha ⁻¹ year ⁻¹)		
	Arsenic	Cadmium	Lead	Arsenic	Cadmium	Lead
U.S.S.R.	2012	816	43824	5	2	78
F.R.G.	728	328	9308	29	13	375
Poland	656	207	4568	21	6	146
Belgium	360	171	3986	118	5	130
France	228	170	10545	4	3	182
Bulgaria	152	67	2234	13	6	201
Austria	103	137	1933	21	6	146

danger to ecosystems caused by the present excessive amounts of trace elements in soils, for example mercury, lead, cadmium, zinc, copper and fluorine. Elements such as nickel, chromium, vanadium, beryllium, arsenic and boron may also be present as contaminants, but their harmful effect is generally local and their effect on soil processes is not fully understood.

About 83% of cultivated soils in Poland are acidic (including 58% very acidic and medium-acidic soils). This situation is mainly due to the interaction of sulfur and its compounds deposited on the ground together with other atmospheric contaminants. Other contributing factors are the incorrect application of acidic mineral fertilizers, as well as insufficient use of lime and calcium-magnesium fertilizers.

Excessive amounts of hydrogen ions reduce the nutrient adsorption capacity of soils. The mobility of aluminum ions in acidic soils exerts a toxic action on plants and limits the biological activity of soils. Nearly all contaminants (elements and compounds) are mobilized in acidic soils. Hence they are more easily transferred to surface waters and also become more available to plants.

It is assumed that the greatest long-term threat is now presented primarily by arsenic, cadmium, lead and mercury. The Polish emissions of the first three metals are comparable to those for highly industrialized European countries (Table 6). Also, the relative emission, calculated per unit of surface area, places Poland in the forefront.

The highest concentrations were found for cadmium, lead, copper and zinc. These concentrations occur mainly in soils in the vicinity of industrial emissions, primarily from non-ferrous metal smelters (Table 7). However, because of the long-range transport of atmospheric contaminants and the application of agricultural chemicals, increased amounts of these metals also appear in soils of rural regions. In addition, vegetable gardens are often associated with the improper use of wastes or composts from communal sewage, the metal contents of which are not controlled, and the use of which can result in considerable local accumulation in soils.

As a result, high concentrations of cadmium are often found in products of

TABLE 7

The highest recorded concentrations of some metals and fluorine around smelters in Poland in comparison with background levels [2]

Element	Concentration (mg kg ⁻¹ soil)	
	Contaminated soil	Background
Cadmium	290	0.1-0.5
Copper	1200	5-15
Lead	4650	20-30
Zinc	10000	25-90
Fluorine	13200	70-250

plant origin. Other trace metals are not so readily absorbed by plants, therefore they are not found in such high concentrations in plants.

Pesticides are indispensable chemical agents for agriculture, providing for the protection and cultivation of plants. An essential safety condition is the introduction of compounds which degrade rapidly in soils, and the observation of the manufacturers' instructions for their use.

In 1982, residues of pesticides based on stable polychlorinated hydrocarbons (e.g. DDT) were found in 85 tested soil samples, despite the fact that these pesticides were withdrawn from use in Poland in 1976. Residues of other pesticides do not seem to remain for so long in the soil. However, only the widespread use of readily degradable compounds (for instance, herbicides from phenoxy acids) will ensure the complete elimination of danger.

Polycyclic aromatic hydrocarbons (PAH) are formed by the incomplete combustion of carbon fuels. Small amounts appear in all smoke-cured food products.

Emission of these compounds by industry presents a particular threat to soils and plants, since they are relatively stable, insoluble in water and of a viscous, tarry nature. These compounds remain for a long period on the surface of the soil and on plants, and present an additional danger because of adsorption of other contaminants.

Because of analytical difficulties, only a few Polish laboratories undertake studies of PAH in soils. Soils in the vicinity of metal smelters and electric power stations contain increased amounts of PAH, on average 100 times higher than their background level. Increased concentrations of pyrene, benzopyrene and fluoranthrene, in particular, are observed.

Chemical degradation of soils proceeds particularly rapidly if the trace elements introduced into the soil remain in a form (or change into a form) which is readily soluble. Their concentration in the aqueous phase of soils increases and, as a consequence, they readily undergo bioaccumulation and migration to surface waters.

The degree of harm caused by trace element contamination depends to some extent on the soil properties. All soils with a large adsorption capacity with

respect to cations are capable of strongly binding these elements and retaining them mostly in the surface levels. These are soils of heavy mechanical composition, large organic matter contents, large amounts of iron and manganese compounds, and large quantities of carbonates and phosphates. However, such soils undergo gradual chemical degradation; degradation proceeds slowly, but is very often irreversible. Therefore, the effects of the contamination of such soils with trace elements appear at a later date.

Sandy soils, with a small adsorption capacity and usually acidic, weakly adsorb trace elements; these are available to plants and can rapidly find their way to surface and groundwaters.

The ability of a soil to retain trace elements depends also, to a large extent, on the use to which the soil is put. Trace elements are retained much more by soils of forest ecosystems than they are by soils of agricultural ecosystems.

CHEMICAL CONTAMINATION OF FOOD

Food, similar to water and air, is a basic element for the functioning of all living organisms. Its quality is associated with the quality of the environment, and also with the activities of man.

In Poland, few attempts have been made to correlate environmental contamination (air, water and soil) and food quality. However, exceptions are found. Examples are studies concerning the contamination of the environment, including food, of areas adjacent to large industrial plants which emit dust and gases to a degree invoking fears both in the population living in such areas, and the local and central authorities.

It follows from the available publications in this field, particularly those from heavily contaminated areas such as Upper Silesia, Rybnica, Cracow and Legnica-Glogow, that the production of food and fodder should not take place in such regions. These regions should be reserved for the cultivation of plants that do not accumulate, to a great extent, contaminants from atmospheric deposition or from the soil.

National control organizations — the National Sanitary Inspection and the Veterinary Sanitary Inspection Boards — test consumer food products to check if their health quality satisfies the governing norms.

Monitoring studies of certain food contaminants considered to be of prime importance (chloro-organic pesticides, lead, cadmium, mercury, nitrites and nitrates) performed under sponsorship of WHO and FAO, allows estimation of the degree of contamination of generally used food products. Unfortunately, these studies are not correlated with concurrent studies of the other two elements of the environment, air and water, which may increase the risk of exposure of the population to these substances.

It is necessary to stress that the consumption of food which contains chemical impurities, as distinct from microbiological impurities, relatively rarely causes immediate acute symptoms of poisoning. We are all exposed to their slow continuous action, arising from accumulation in the body of

microdoses taken daily. It must also be taken into account that reactions of certain substances with other components in the system may lead to the formation of much more toxic compounds, sometimes of a carcinogenic nature.

CAUSES AND SOURCES OF FOOD CONTAMINATION

Pollution of the environment is very extensive in Poland. Acid rain causes mobilization of metals from the soil by releasing soluble compounds which are more readily absorbed by plants. Therefore, plants grown in fields and gardens located in ecologically endangered regions are of particular concern. The products are often consumed by the family of the producer, and are not transported elsewhere. Studies performed by sanitary — epidemiological stations and the Institute for Environmental Management show that such products are high contaminated. In particular, vegetables contain large amounts of metals. Concentrations of metals in vegetables from the vicinity of the zinc and lead works in Boleslawiec and Miasteczko Śląskie are: lettuce, 4 mg Cd kg⁻¹, 69 mg Pb kg⁻¹ and 393 mg Zn kg⁻¹; carrots, 4 mg Cd kg⁻¹, 57 mg Pb kg⁻¹ and 194 mg Zn kg⁻¹.

In the family gardens traditionally cultivated in Upper Silesia, the contamination of vegetables with heavy metals considerably exceeds the national average. If we consider the fact that, for most of the year, the families of the owners of these gardens consume mainly their own products, we can see that exposure to contamination is very great in that area.

Impurities related to agricultural activities are a very important element of food contamination in non-industrialized areas. Intensification of agricultural production requires increased fertilization. Quite often, mineral fertilizers, particularly phosphate fertilizers, contain large amounts of metals. These contaminants enter plants and water and, through the food cycle, invade the body of man. Application of excessive doses of nitrogenous fertilizers causes contamination of ground and surface waters with compounds of nitrogen, and leads to increased amounts of nitrates in plants.

Plant protection agents are also applied in agricultural regions. If these are applied correctly, with observance of the correct dose at the correct interval, residues in food products should not pose a danger. However, these agents are not applied properly by farmers, and thus residues are found in foods.

Animals receive a number of pharmaceutical preparations for prophylactic purpose or as cures. The correct waiting period before slaughter is not always observed, resulting in incomplete elimination of drug residues.

The processing of food products also creates possibilities for their further contamination. Drying of agricultural products in gases can often cause contamination with polycyclic aromatic hydrocarbons (PAH). Similar contamination may also occur during traditional smoke-curing.

It has been proposed that the main source of exposure of man to carcinogenic agents is food. Data presented in Table 8 seem to confirm this.

The materials used for the construction of containers and equipment in the

TABLE 8

Daily exposure of man to carcinogens from various sources ($\mu\text{g day}^{-1}$) [6]

	Benzo[a]pyrene	Carcinogenic hydrocarbons	Total PAH
Air	0.0095–0.0435	0.038	0.207
Water	0.0011	0.004	0.027
Food	0.16–1.6	No data	1.6–1.6

food industry may be a source of metals via migration. Canned food may be exposed to metal contamination by this route. Plastic packing materials, rubber gaskets, coatings and lacquers may contain low-molecular-weight compounds which can contaminate food products. Such low-molecular-weight substances may be monomers, softeners, stabilizers, conservation agents, vulcanization accelerators, solvents or coloring matter. These substances, in addition to their harmful effects, can negatively affect the organoleptic properties of products.

EFFECTS OF FOOD CONTAMINATION

Consumption of food containing trace amounts of heavy metals, which undergo bioaccumulation, may lead to irreversible effects on health. The Expert Committee of the FAO/WHO has established a weekly tolerable dose for an adult of 3000 μg lead and 400–500 μg cadmium.

TABLE 9

Weekly consumption of lead (μg) by persons 14–18 years old [7]

City	1982				1983			
	<i>x</i>	<i>m</i>	<i>d</i>	<i>N</i>	<i>x</i>	<i>m</i>	<i>d</i>	<i>N</i>
Białystok	819	220	2394	4234	733	175	2136	13500
Ciechanów	1767	514	4033	8701	74	140	291	711
Kielce					140	140	140	140
Kraków					3017	2071	4262	5505
Lublin	613	515	1654	2585	1079	621	2878	6516
Olsztyn	861	483	2450	4060	654	315	1715	7140
Opole	1532	1227	3332	12740				
Płock	1164	1134	3024	3703	59	210	1127	1540
Rzeszów					1309	1151	2648	3010
Sieradz	789	245	2524	15453	320	210	1200	5725
Skierniewice	140	140		140	239	140	1144	1505
Słupsk	935	790	2191	4340	1737	190	7283	9517
Wałbrzych	2921	1295	12145	14231	5479	1406	18502	25631

Assumed tolerable dose, 3000 μg /person/week. *x*, arithmetic mean; *m*, median; *d*, value below which 90% of the data occur; *N*, highest recorded value.

TABLE 10

Weekly consumption of cadmium (μg) by persons 14–18 years old

WSSE	1984				1985			
	x^a	m	d	N	x	m	d	N
Białystok	405	349	1001	1498	260	78	889	1141
Kielce					898	616	1629	2909
Kraków	171	155	388	601	694	560	1659	2842
Lublin	420	105	126	520	361	105	1332	2310
Olsztyn	127	70	1313	4200	229	70	665	2688
Płock	1223	1023	2919	5136				
Rzeszów	327	320		588	698	416	1741	3906
Sieradz	70	70	70	70	146	105	653	1207
Słupsk	300	250	924	1155	533	386	1823	2926
Wałbrzych	2073	887	6488	6650				

Assumed tolerable dose, 400–500 μg /person/week.^aSee Table 9.

During the years 1982–1985, the National Institute of Hygiene and the district sanitary and epidemiological stations studied the actual intake of lead, cadmium and mercury by youths and small children on the basis of concentrations of these metals in daily meals. Diet studies provide a more complete picture of the consumption of metals, since they take into account their presence in water and, to some extent, in air, as well as their migration from kitchen and table utensils and the effect of culinary processes. The examined meals were consumed four times per day for 10 consecutive days. The results obtained for lead and cadmium are presented in Tables 9 and 10. It is apparent from these tables that the allowable weekly consumption is often exceeded.

Barylko-Pikielna [6] evaluated the annual intake of mercury, lead and cadmium from the consumption of two different diets, average and special. The study indicates that the maximum allowable intake was exceeded for cadmium and mercury, but lead was within the established limits (Table 11). The main sources of metals are products which are usually consumed in the largest

TABLE 11

Estimated annual consumption of heavy metals in food [6]

Metal	Annual consumption (mg/person)		
	Maximum allowable dose based on WHO standard	Average	Highest
Hg	15.6	15.6	29.4
Pb	182.0	73.8	139.0
Cd	23.4	16.9	31.4

TABLE 12

Nitrate content of vegetables (A. Bronowska-Senger, 1986) [8]

Product	Range (mg NO ₃ kg ⁻¹)
Potatoes	12.5-488
Carrots	847-1557
Cabbage	366-1624
Onions	112-455
Lettuce	89-3498
Radish	247-4338
Beets	699-6890
Tomatoes	17-170
Spinach	76-1421
Cucumbers	59-611

quantity (potatoes and baked foods) or those which are significantly contaminated (meats).

Excessive nitrogenous fertilization results in the accumulation of nitrates in vegetables and high nitrate concentrations in potable waters. Table 12 reports the range of nitrates in vegetables.

In food centers in Poland, analyses are carried out for pesticide residues. Table 13 shows, as an example, the percentage of samples of animal origin, tested in the years 1980-1985, which exceeded the allowable level of chloro-organic insecticide residues. The tolerance limits were taken according to the proposed, but not yet accepted, allowable levels. These are, for milk, 1.25 mg DDT kg⁻¹, 0.2 mg γ -HCH kg⁻¹ and 0.5 mg DMDT kg⁻¹; and for eggs, 0.5 mg DDT kg⁻¹, 0.2 mg γ -HCH kg⁻¹ and 0.5 mg DMDT kg⁻¹. The prohibition, in 1976, of the use of DDT in Poland resulted in generally lower levels of residues of this pesticide in food products. γ -HCH and DMDT were found in highest concentrations in raw milk. The reason for this was probably the use of these agents, particularly γ -HCH, to sanitize cow sheds. Table 14 gives an estimation of the yearly intake of chloro-organic pesticides from food.

It is worth noting that processing food for export has a very positive influence on food quality in Poland. There are specially designed areas and plants for processing food for export which are under strict analytical control. Laboratories founded for export purposes are also mainly responsible for upgrading food quality for sale within the country.

CONCLUSIONS

The Polish environment is contaminated to such a degree that the biological existence of the nation is threatened.

The characteristic negative feature of the Polish economy is its very high energy consumption. This is particularly evident when we relate the amount of contaminants discharged into the air, water and soil to the production of one

TABLE 13

Percentage of samples exceeding the allowable level of chloro-organic insecticide residues (1980–85)

Product	Year	Percentage of samples above the allowed level		
		DDT	γ -HCH	DMDT
Milk for consumption	1980	2.90	1.50	
	1981	1.83	4.12	2.27
	1982	2.33	4.32	2.65
	1983		4.46	3.15
	1984	0.95	1.58	4.10
	1985	3.63	2.48	
Raw milk	1980	18.70	14.70	
	1981	0.96	14.43	16.35
	1982	4.22	9.86	16.91
	1983		15.00	15.00
	1984		27.08	20.84
	1985	1.43	7.14	4.28
Milk products	1980		3.60	
	1981			
	1982		1.52	
	1983			
	1984	2.75		
	1985	2.66	5.46	
Powdered milk	1980	6.20	4.10	
	1981	0.95	11.40	1.90
	1982		2.19	6.57
	1983		10.04	
	1984	0.57	5.75	0.57
	1985			
Eggs	1980	5.10	1.50	
	1981		0.76	
	1982	1.04	0.35	
	1983	1.01		
	1984			
	1985		4.10	

Allowable residue levels (mg kg^{-1}): milk and its products, DDT 1.29, γ -HCH 0.2, DMDT 0.5, recalculated for fat; eggs DDT 0.5, γ -HCH 0.2, DMDT 0.5.

TABLE 14

Estimation of the annual consumption of chloro-organic insecticides in food (mg/person/year) [6]

	Average	Highest	Allowable
DDT	18	140	128
HCH	10	70	155

^a Allowable standard according to WHO.

U.S. dollar towards the GNP. To produce one U.S. dollar Poland consumes 2.27 kg of fuel, while in Western Europe it varies between 0.5 and 0.6 kg. Another factor is the over-developed, but not yet modernized, heavy industry.

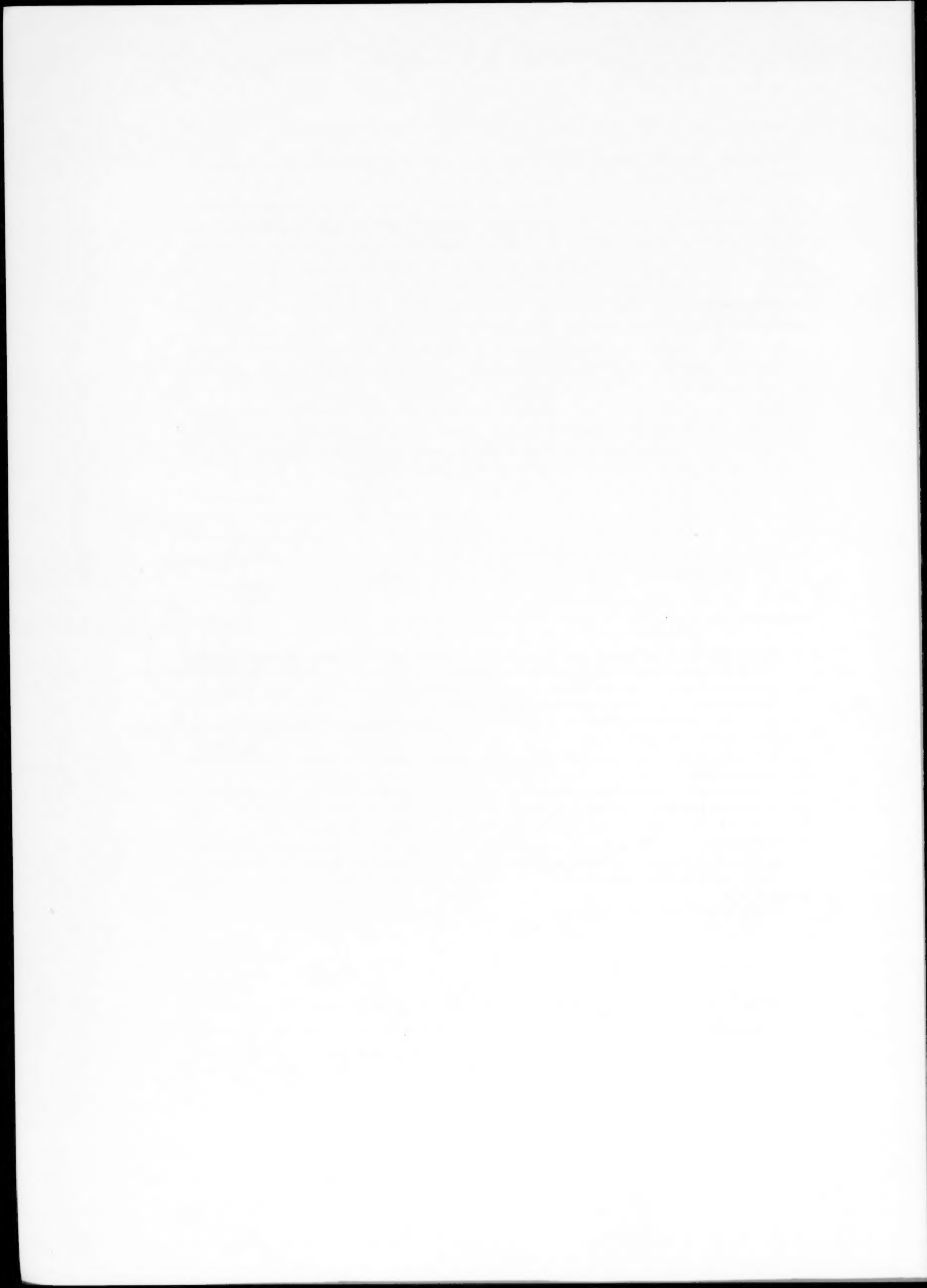
Parallel to this grave environmental situation there also exists a serious economic crisis which limits possible solutions to environmental problems, especially since the problems were hidden for a long period. Therefore, a national industry capable of manufacturing suitable equipment for environmental restoration has not been developed. The other solution, involving purchase from abroad, is very limited due to shortage of hard currency.

However, recent events give rise to hope. Both the Solidarity-based opposition and the Government have rapidly come to agreement on environmental issues.

Although there is a real attempt to improve the situation, significant changes should not be expected in the next few years without international assistance. There are also unsolved problems concerning the influx of SO_2 and other pollutants from other countries. Poland also exports air pollutants to other countries, but receives as much as 50% of its SO_2 deposition from outside its borders, mostly from Czechoslovakia and the DDR. No real changes are yet noticeable in either of these countries in their attitudes towards the environment. Therefore, it is likely that, during the next one or two decades, coniferous forests will disappear in large parts of Central Europe.

REFERENCES

- 1 The Polish Chemical Society Report Chemiczne zagrożenia środowiska w Polsce (Chemical Threat to the Environment in Poland), Lublin, 1984.
- 2 The Polish Chemical Society Report Chemiczne zagrożenia środowiska w Polsce (Chemical Threat to the Environment in Poland), Lublin, 1987.
- 3 GUS Report Ochrona Środowiska i Gospodarka Wodna (Environmental Protection and Water Management), Warszawa, 1987.
- 4 J. Kapala, in Proc. 2nd Symp. "Chemiczne Zagrożenia Środowiska w Polsce", Lublin, 15-18 October 1986.
- 5 Z. Kozak and J. Szczypa (Eds), Chemiczne zagrożenie środowiska w Polsce, Lublin, 1987.
- 6 N. Baryłka-Pikielna, Evaluation of the Level of Contamination of Food as a Result of the Contamination of the Environment, Polish Academy of Science, Warszawa, 1986.
- 7 National Institute of Hygiene and district sanitary and epidemiological stations, unpublished. A. Bronowska-Segner, in Proc. 2nd Symp. "Chemiczne Zagrożenia Środowiska w Polsce", Lublin, 15-18 October 1986.



ACID PRECIPITATION MONITORING AND RESEARCH. REVIEW OF CURRENT NORWEGIAN ACTIVITIES

GEIR TAUGBØL

Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo 3 (Norway)

ABSTRACT

Acid precipitation is a major threat to Norwegian ecosystems. Damage to aquatic biota has occurred in large areas of southern Norway, deterioration of vegetation and forest is expected to develop, and human health may be affected. Apart from the short-term economical losses, the negative development of environmental quality is giving rise to public concern. Politically and administratively, the issue has been given top priority among environmental issues for nearly 20 years. Hence, fairly large resources are spent on monitoring and research activities, reduction measures and local ameliorating countermeasures.

During the seventies, a joint, interdisciplinary research and monitoring project was carried out to establish basic knowledge of the cause/effect relationships and the extent of the problems caused by acid precipitation. From 1980 onwards the activities were continued within a separate monitoring programme and within different research projects which comprised part of the general scientific activity. The monitoring program is administratively and thematically divided into four major categories emphasizing air processes, water, aquatic fauna, and forest and vegetation. The main purpose of the programme is to reveal the temporal trends and to assess the geographical distribution of effects.

The deposition of most pollutants, except NO_x , peaked during the late seventies, though the levels are still at the same order of magnitude. The acidification of soil and waters, in terms of loss of acid neutralizing capacity, has tended to increase during the last decade, at least in the impacted areas of southernmost Scandinavia. The damage to aquatic fauna is still increasing, wiping out additional numbers of fish stocks every year. Severe impact on forest and vegetation is feared and the data from 1987 indicate that damage already occurs in some areas.

Research projects are carried out on nearly every aspect relevant to acid precipitation. Priority has been given to research areas with the most severe effects and where considerable lack of knowledge is evident. Present high priority areas are: photo-oxidants and nitrogen compounds, transformation processes and effects; mechanisms, dose/response relationships for acidification/recovery of soil and waters; effects on forest and vegetation; effects of aluminium; and restoration of fish stocks.

Norwegian scientists cooperate extensively with groups in other countries and participate in international monitoring networks and research programmes.

INTRODUCTION

In the 1920s, abnormal recruitment failure, first discovered in salmon hatcheries in southernmost Norway, was suspected to be caused by acidic water. The hypotheses concerning correlation to acidic deposition were not validated until the late fifties and sixties when the damage to fish stocks also

became increasingly apparent. In the seventies, the concern about the acid rain problem became an important political and administrative issue. A comprehensive research programme, the SNSF project ("Acid Precipitation: Effects on Forest and Fish") (Overrein et al., 1980), was launched to provide systematic scientific knowledge. This project ran through the years 1972–1980.

One important conclusion from this joint, interdisciplinary project was that, during the last decades, acidification of surface waters due to acid deposition had occurred throughout large areas of southernmost Norway. Disturbances of aquatic ecosystems, including extensive loss of fish stocks, were caused by acidic waters. The project also concluded that prolonged deposition of acid components might change the soil properties and influence forest growth and vigour.

Since 1980, the research and monitoring activities, which had evolved during the SNSF project, have continued in a separate monitoring programme and within numerous research projects. The problems caused by acid rain are still increasing, damage to aquatic life being the most obvious effect. However, during the last 2 years effects on forests are also suspected.

By Norwegian standards, a considerable amount of money has been spent on acid precipitation topics. In 1988, the grants for monitoring and research were approximately \$2 million and \$4 million, respectively. In addition, some \$2.5 million is spent on measures to mitigate the effects, such as liming surface waters and restocking fish. A number of volunteers are also spending substantial resources to try to restore their local environment.

MONITORING

The Norwegian monitoring program for long-range transported air pollutants is divided into four major parts emphasizing *air and precipitation*, *surface and groundwater*, *fish and invertebrates*, and *forest and soils*. The stations and field sites are located throughout Norway, but a denser network is found in the southern regions where the most serious impacts are found. Figure 1 shows the location of sites and the monitoring elements included.

The State Pollution Control Authority (SFT) conducts the programme, contracting different institutes to run the various parts. The existing programme started in 1980, though some of the elements have evolved from activities dating back to the sixties and seventies. There are some additions and changes to the programme to fit the requirement for relevant data as demanded by increasing concern about, for example, forest damage, ozone effects and increasing nitrogen loadings.

A short description of the present programme with some results from 1987 (1988 data are not yet reported) is given below. Administratively the programme is divided into four parts, namely air and precipitation, water and groundwater, aquatic fauna and forest and vegetation. The results are reported yearly (SFT, 1987a, 1988a, 1989) in Norwegian with a short English summary. A report in English was issued in 1986, reviewing the results from the years 1980–1984 (SFT, 1986).

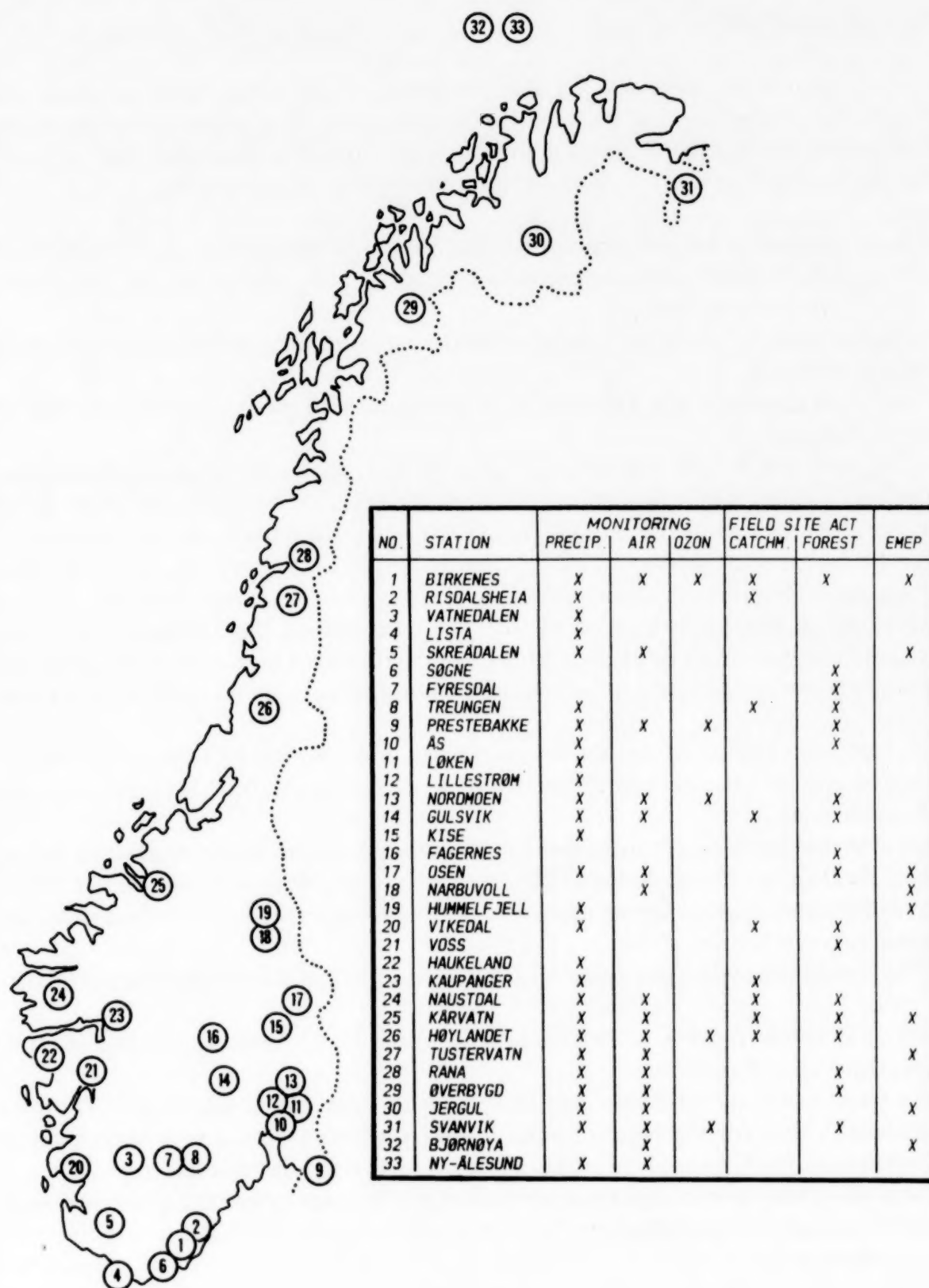


Fig. 1. Monitoring and research sites throughout Norway.

Air and precipitation

The Norwegian Institute for Air Research (NILU) has been awarded the contract to conduct this part of the programme. The original network for monitoring background air and precipitation quality was designed to yield data for assessment of the long-range distribution of pollutants:

- Daily records of air and precipitation chemistry were taken at 10 stations in 1987, including all main components such as H^+ , SO_x , NO_x , Ca, Mg, NH_3/NH_4 , Na, Cl and conductivity
- sulphur dioxide and particulate sulphate concentrations were recorded daily at six stations
- the trace elements Pb, Cd and Zn in precipitation were recorded weekly at four stations.

The network is continuously being extended, partly because an increasing number of other activities are dependent on reliable background data. Such supportive stations are located so as to provide data which can be interpreted together with some observed effects, for example on vegetation, water quality or aquatic organisms. The sampling procedure at these stations varies according to the requirements of the other activities, but includes the main components, recorded weekly or at higher frequency. Obviously such data add to the regular air and precipitation monitoring, giving a more efficient system:

- in 1988, the complete network relevant to monitoring of long-range transported air pollutants amounted to 29 stations (including Spitzbergen and Bear Island)
- nine of the stations are included in the network of the European Monitoring and Evaluation Programme (EMEP) (see Iversen, this volume, pp. 87-99).
- five stations included ozone monitoring. The number will soon be extended to nine.

The results show some trends which are not always statistically significant:

- the SO_2 levels tended to decrease from 1979 until 1983; the trend is now levelling out (Fig. 2)
- the sulphate concentration has been slowly decreasing since 1979. This is especially true for the level of particulate sulphate in the air. A less obvious decrease is recorded for sulphate concentration in precipitation
- each year, nitrogen compounds show a slight increase over the previous year
- heavy metals in precipitation have been decreasing substantially since the mid-seventies.

The observations are readily explainable as a result of changes in emissions in Europe during the last 5-10 years.

Generally, the southernmost parts of Norway are receiving the heaviest loads of long-range transported pollutants due to the short distances from Central Europe, whereas western Norway has very high annual precipitation

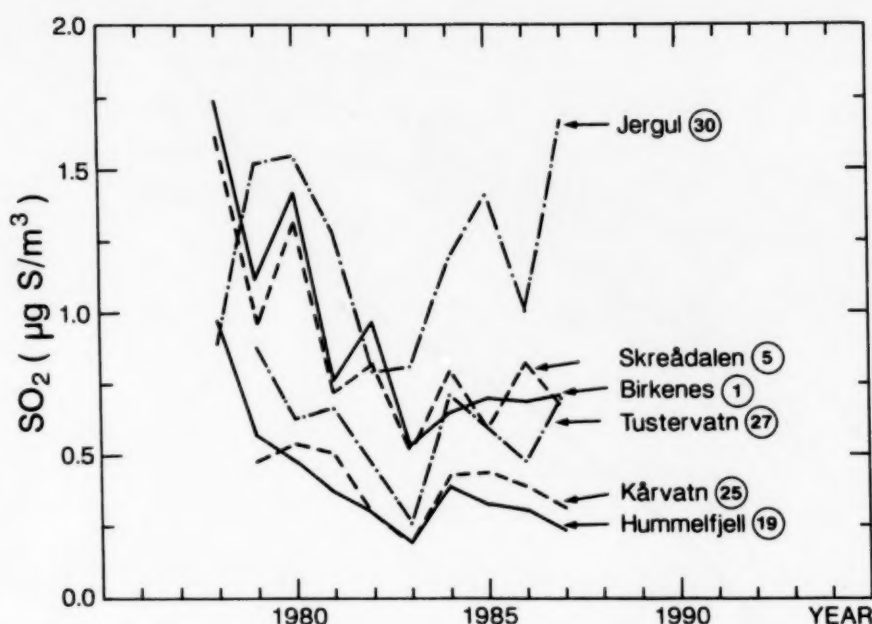


Fig. 2. Yearly average concentrations of sulphur dioxide in the air. Stations refer to Fig. 1 (from SFT, 1988a).

giving considerable wet deposition. The area in the far north around Station 31 (Fig. 1) is strongly influenced by a large nickel smelter to the east, across the U.S.S.R. border, resulting in high SO_2 levels and high deposition of metals. Figure 3 shows the distribution of wet H^+ deposition throughout Norway in 1987.

Water and groundwater

The Norwegian Institute for Water Research (NIVA) is responsible for this part of the programme. The activities include:

- Monitoring of 16–20 rivers (dependent on yearly funding) in southern Norway and one river in a pristine area in mid-Norway. These rivers are selected because of sensitive water quality and/or their importance as salmon rivers. They are sampled monthly with weekly samples taken during the snowmelt period and are analyzed for pH, conductivity, Ca, Mg, Na, K, Cl, NO_3 , SO_4 , TOC, Al (also fractions) and alkalinity. Data exist back to 1966 for some of the rivers, giving reasonable periods for trend analyses.

The data show a general increase in acidification (observed loss of alkalinity) since the sixties. Since 1980, the rivers along the southern coastline show stable and chronic acidification, while the western rivers are still losing their acid neutralizing capacity. The sulphate levels, however, show some downward trends during recent years, probably reflecting somewhat less sulphur deposition. On the contrary, the nitrate levels show a general upward trend in the south and southwest of the country. Other data (1000-Lake Survey, below) confirm this alarming nitrate tendency (SFT, 1987b).

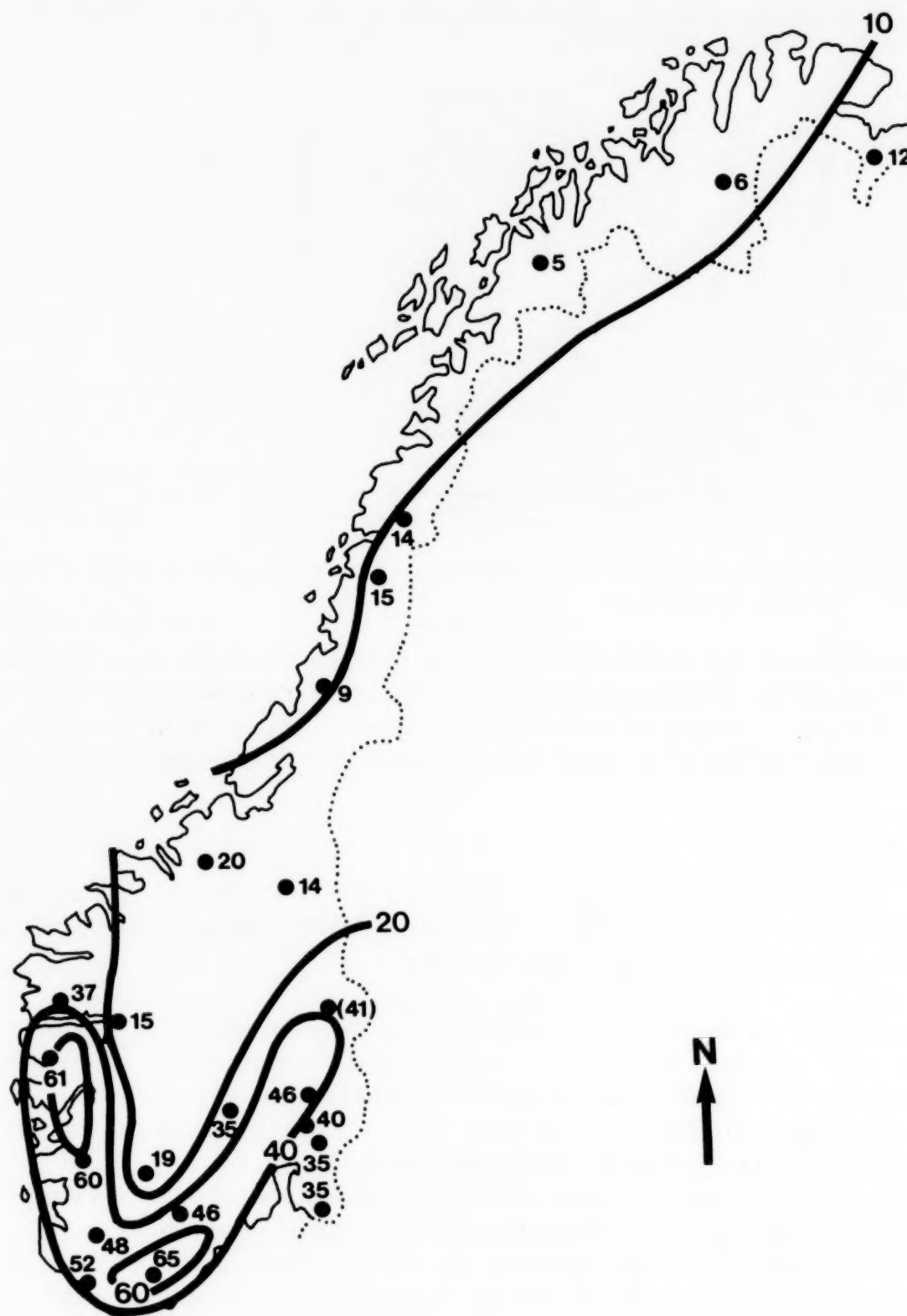


Fig. 3. Wet deposition of strong acid (H^+ , $meq\ m^{-2}$) during 1987 (from SFT, 1988a).

- Calibrated catchment studies are carried out at four sites which are followed on a yearly basis. Small headwater catchments are monitored to obtain trends in status of acidification and to clarify the major processes involved.

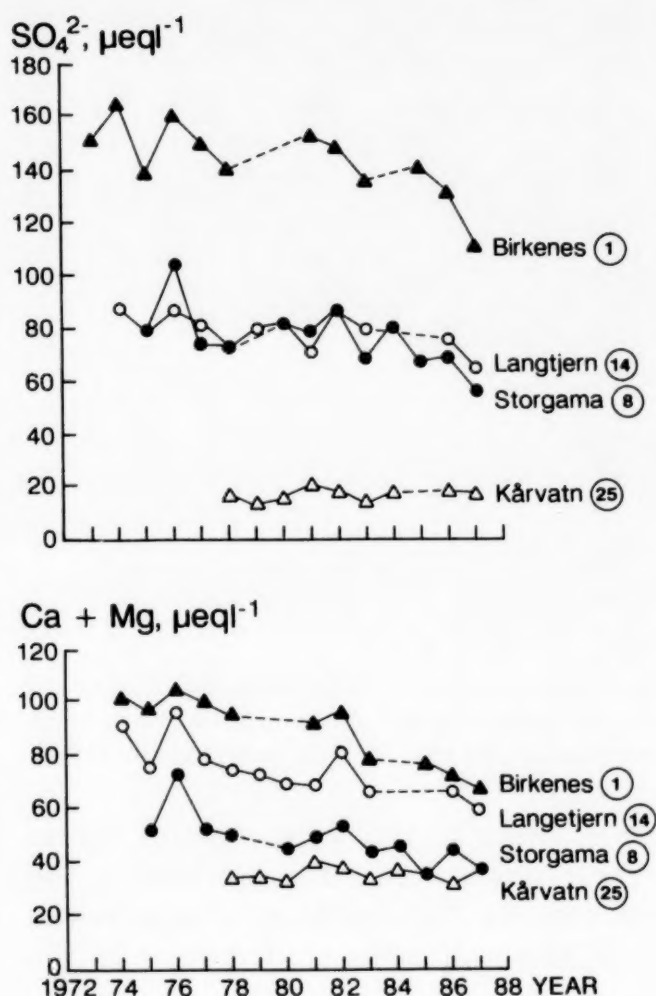


Fig. 4. Yearly average concentrations of sulphate (upper) and sum of Ca^{2+} and Mg^{2+} in runoff from four catchments. Stations according to Fig. 1 (from SFT, 1988a).

There is a tendency to a reduced content of sulphate in runoff from catchments in southern Norway, and a parallel increase in aluminium and a decrease in base cations (Fig. 4).

– Groundwater is studied in five reservoirs in eastern, southern and western Norway, near the calibrated catchments. They are sampled yearly and analyzed for the components mentioned earlier.

The groundwater is generally rich in aluminium where there are significant loads of acid precipitation, i.e. in eastern, southern and south-western districts. In some areas the sulphate concentrations are high, while pH and Ca are low.

– In 1986, an extended survey of lakes was carried out throughout Norway (Rosseland and Henriksen, this volume, pp. 45–56; SFT, 1987b). One thousand and five lakes were sampled and analyzed for pH, SO_4 , NO_3 , Ca, Mg, Na, Cl, Al (also fractions) and TOC; 305 of the lakes were also sampled in 1974/75 allowing comparative studies.

The survey gives an excellent database for assessment of the current

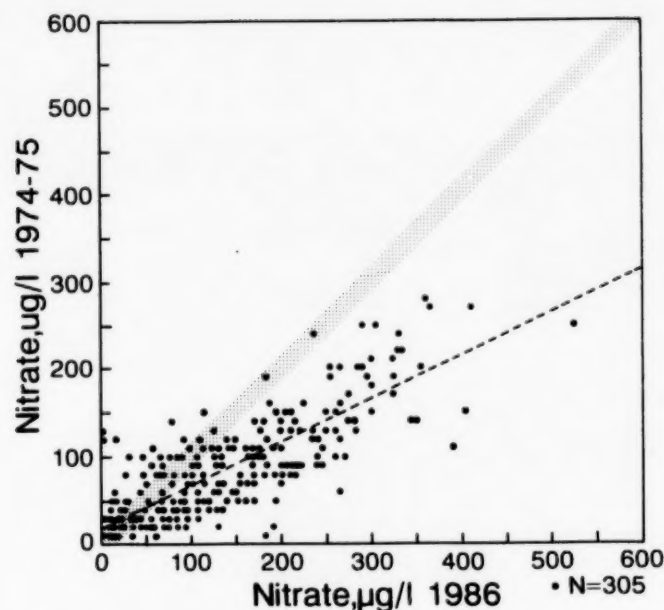


Fig. 5. Nitrate values in 1986 in comparison with conditions in 1974-75 for 305 lakes in southern Norway. Regression line is: $y = 20 + 0.49x$ ($r = 0.75$). Lakes that fall above or below the hatched zone had lower or higher concentrations, respectively, in 1986 than in 1974-75 (from SFT, 1987b).

situation and the search for trends. It is also a unique reference for future surveys. One especially alarming observation is the increase in nitrate in the most acidified lakes in the southernmost regions. This could be interpreted as an increasing leakage of nitrate through the soils, thus contributing to the acidification of waters (Fig. 5).

- In addition to the chemical analysis, all the lakes were investigated with respect to their biological status, i.e. fish stocks and, in some cases, invertebrates (SFT, 1988b). The methods used included interviews with landowners and fishermen about catches and the sampling of plankton and bottom fauna with nets. A system for classifying acidification according to the population of species of invertebrates has been developed (Fjellheim and Raddum, this volume, pp. 57-66). As this system supplements the chemical analyses, it has proven to be a very valuable method for assessing acidification status.

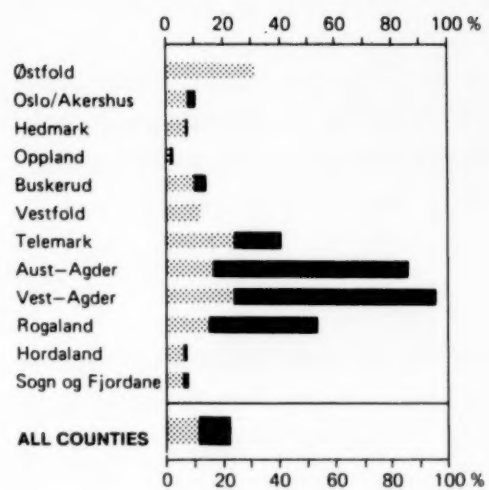
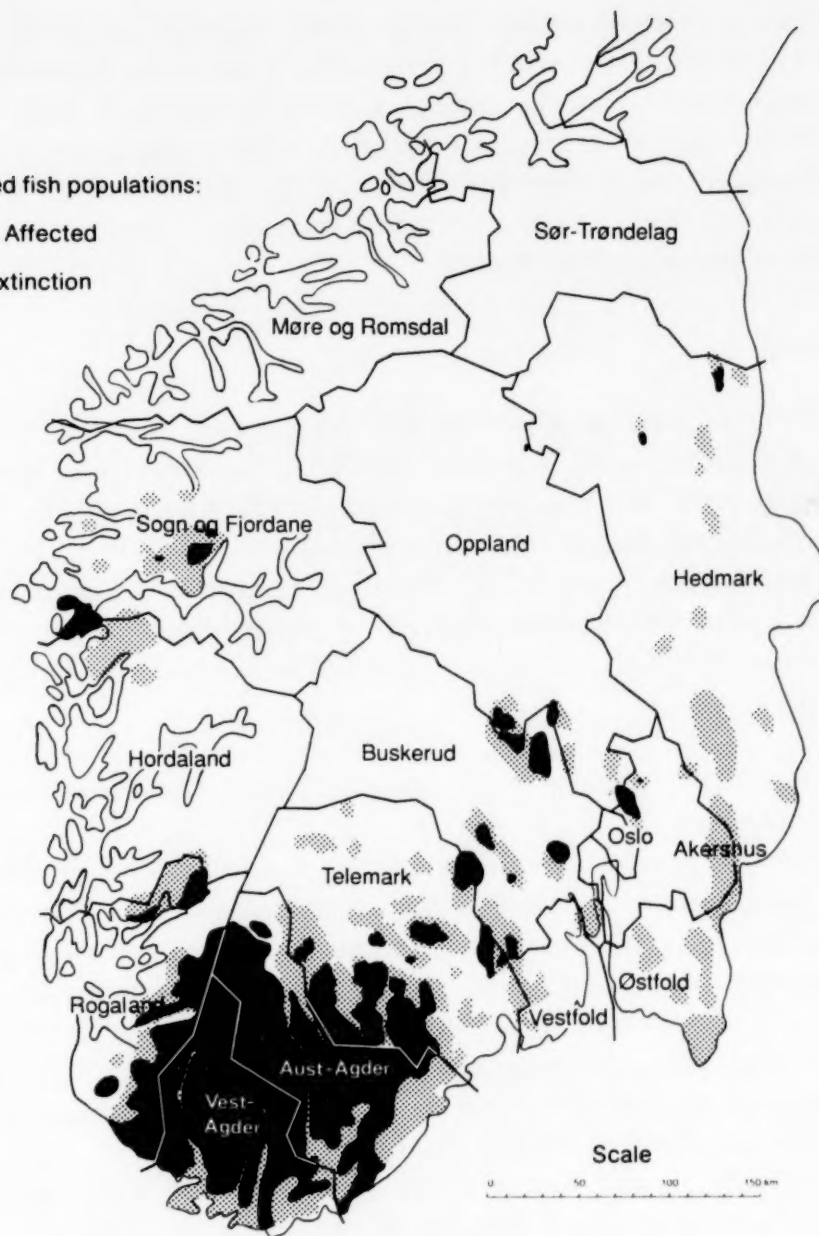
The biological status was formerly assessed during 1971-75 for 254 of the lakes. Generally, the damage to aquatic life has increased since that period. The loss of trout stocks in the heavily affected areas in the southernmost parts has increased from 30 to 64%. The area showing serious biological damage has grown from 33 000 to 36 000 km².

Fig. 6. Areas in southern Norway in which fish populations are affected by acidification. This map is an updated version of the SNSF map from 1974-79. Revisions are based on information from Annual Reports from the Norwegian State Pollution Control Authority and from the 1000-lake survey. The relative sizes of the affected areas within each county are shown in the bar diagram (from SFT, 1988b).

Areas with affected fish populations:

Strongly Affected

Virtual Extinction



This large database shows very good agreement between chemical parameters in the lakes and the loads of acid components deposited through air and precipitation onto the catchment area. The southern regions of Norway receive by far the largest amount of acid deposition and, quite consistently, the same regions have the lowest lake pH and the highest lake aluminium and sulphate levels. In turn, the acidification manifests itself in a corresponding deterioration of aquatic life (Fig. 6).

Aquatic fauna

The activities of this programme are the responsibility of the Norwegian Institute for Environmental Research (NINA). The 1000-Lake Survey included aquatic fauna as well, but this was a special study which will be repeated after a long interval, NIVA having the main responsibility. The biological response is changing more slowly than the chemical response, thus only some of the monitoring sites for most elements of this programme are investigated each year. After some years, the sites are sampled again to reveal time trends. The main elements are:

- surveying the invertebrate communities, using the classification method described above
- assessing the fish stocks in selected areas (counties) by interviewing local fishermen, landowners or other informed persons
- test fishing with nets and electricity for more thorough investigations of fish populations and the correlation with chemical parameters. Population parameters such as growth, age composition, spawning activity, recruitment, food availability, etc., are recorded.
- regional surveys of selected main watersheds with emphasis on density of fish, recruitment, changes in fish populations, etc.
- some selected salmon and sea trout rivers are studied, with special emphasis given to the recruitment and density of juveniles (0+ and 1+ years old)
- 100 lakes from the 1000-Lake Survey have been selected for further investigations. The biological status of a number of these lakes will be updated each year.

The results show mainly that the biological system is not in equilibrium with the present acid loading. The damage is generally increasing, most apparently along the border of existing problem areas. In some moderately impacted areas, however, there are signs of improvement in recent years.

Forests

The Norwegian Institute for Forest Research (NISK) conducts this part of the monitoring programme in cooperation with the Norwegian Institute of Land Inventory (NIJOS). NILU provides the meteorological data along with data on air quality and deposition of pollutants. The programme was launched

in 1985. The size of the project is growing very fast, since concern about forest damage has increased considerably in recent years, though extensive damage has not yet been observed. However, some data reported for 1988 show a negative development since 1985. The monitoring plots are located in coniferous forests, which is economically by far the most important forestry in Norway. In 1987 the activities were:

- intensive investigations of 17 permanent plots, 25×25 m, located throughout the counties of Norway. Vitality characteristics such as crown density and colour are observed, together with investigations of litterfall, soil solution, and physical and chemical soil properties. There are also analyses of needle waxlayer, root and needle morphology and composition
- the forest ecosystem has, of course, a number of interacting components, making many different records of interest or necessary. Nevertheless, some priorities have to be given. Factors such as fungi, insects, ground vegetation and lichen are emphasized
- air and precipitation quality parameters are needed, since these factors are the hypothetical cause of possible future damage. Therefore, the plots are located in association with an existing monitoring station or a new station is installed, run by NILU
- beside these sophisticated investigations at a limited number of plots, there are less detailed studies at some 800 plots, focusing on visible tree health parameters. The large number of plots will provide a reasonable database for statistical analyses. In some of the plots more detailed investigations of soil and vegetation are also carried out. NIJOS has the responsibility for this part of the programme
- in addition, the ongoing national forest surveys also provide results for monitoring of acid precipitation effects. The primary aim of this survey has traditionally been related to commercial use of the timber. The "new" forest damages reported in Central Europe have made some additional observations desirable. The classification of the forest is now standardized according to the European system and reported to the Food and Agriculture Organisation (FAO) and the Economic Commission for Europe (ECE) within the United Nations.

Damage to forests (or trees) in Norway cannot unambiguously be related to long-range transport of air pollutants. However, in the northernmost county, Finnmark (Station 31, Fig. 1), there is obvious local damage caused by a source some kilometres across the U.S.S.R. border. The results reported by NIJOS for 1988 also indicate increasing damage to the forests of Aust-Agder county (e.g. Stations 1 and 2, Fig. 1) in the southernmost part of Norway. The number of trees with $>10\%$ needle loss has increased from 46 to 69% since 1985, indicating a deterioration of tree health, though more years of study are necessary to verify the possible trend. These results are difficult to relate to a specific factor and more long-term investigations are certainly needed to support any hypothesis. However, combined with a knowledge of high annual

deposition of sulphur and nitrogen compounds and presumably increased soil acidification in the same area, the results could be a warning of impaired forest health.

Due to the complexity of the forest ecosystem and the number of possible influencing parameters, we will perhaps never have direct evidence for the effects of background air pollutants on natural forest stands. Nevertheless, it is valuable to establish a reference from which to assess future changes in forest health and also to provide a database for research activities which might possibly clarify the mechanisms involved.

RESEARCH

Priority of research topics

Since the termination of the SNSF project in 1980, a comprehensive and united "acid rain research project" has not existed in Norway. Research topics relevant to "acid rain" have become part of general scientific activity. However, as "acid rain" is a major environmental threat, management has an urgent need for scientific knowledge in its work against the effects. Therefore, a substantial amount is granted from public funds every year to ensure appropriate activity in "acid rain" research. The Ministry of Environment supported various projects for a total of \$1.5 million in 1988, which was in addition to activities funded by research councils, universities and research institutes.

A coordinating committee was established to give advice about priorities and projects to be supported, thus optimizing the resources available. As a means for evaluation, the committee has formulated a priority programme to rank the topics within acid precipitation research according to lack of knowledge and the current and future importance in terms of possible extent of negative effects. The priorities thus reflect what knowledge is at present most urgently needed as seen through the eyes of management. The programme is intended to be revised every second or third year as new public funds for research activities are applied for by interested scientists and shared among projects which are both in accordance with the given priorities and of appropriate scientific quality.

The priority programme is a systematic method of establishing what research is most urgently needed. To give priorities to various topics, a well-defined method is applied. The process is described very briefly below. The idea is to divide the very complex, interdisciplinary research area into elements suitable for evaluation. The most general division is into categories such as air research, water, health, etc. The differentiation is then made more detailed by referring to various components, such as sulphur compounds, nitrogen compounds, photo-oxidants, aluminium, etc., which are of importance for the area considered. For example, the role played by nitrogen compounds in water acidification is one of the topics considered.

Scientists are asked to help to evaluate the area in which they have expertise. The criteria for evaluation are carefully chosen and explained to ensure an objective and adequate treatment, limiting subjective preferences as far as possible. Weight is given, for example, to current knowledge, known effects within the particular topic, the extent of effects, the economical consequences of the effects and the possible future effects. The persons responsible for each topic are obliged to give a number-value to classify the results of each evaluation. Finally, these points are totalled, expressing the total score for that topic. Then the main conclusions are deduced, expressing the most important efforts to be made.

The current priority programme, which was issued in April 1988, emphasizes the following topics:

- nitrogen compounds; processes in the air and their effects on soils, surface waters and forests
- photooxidants; processes in the air and their effects on forests
- mechanisms and dose/response relationships for acidification of soils and waters, including reversibility and critical loads
- aluminium; effects on fauna (including humans)
- mitigating measures to ameliorate the damage to aquatic fauna.

This is not to say that other relevant topics are scientifically inferior, only that limited resources should be directed to what hopefully will be an optimum result regarding the current needs of management.

In addition to Norwegian funds, there are grants from sources abroad. An example of an international research project is the Surface Water Acidification Project (SWAP), a cooperation between scientists of the U.K., Sweden and Norway. The project is funded from the U.K. and has the aim of understanding the acidification of waters and soils and to clarify the extent of the problem. A consensus has been reached between the participants of the project, forming a very important basis for international agreements on emission reductions.

The Environmental Protection Agency (EPA, U.S.), the U.S. Electric Power Research Institute (EPRI), The Environmental Protection Board of Sweden, Environment Canada and the Ontario Ministry of the Environment (Canada), are also financial contributors to ongoing research activities in Norway.

Ongoing research activities

Atmospheric transport and deposition

The Norwegian Meteorological Institute is the Synthesizing Center West of the EMEP cooperation (see Monitoring, above) and thus handles and interprets results from the EMEP monitoring network. A model for the transport of air pollutants, based on emission data and wind trajectories, has been developed and provides important data for the evaluation of the impact from various sources throughout Europe. Currently, much effort is put into studies which include nitrogen oxides, ammonia and oxidizing reactants in such models (Iversen, this volume, pp. 87-99).

At NILU and the University of Oslo, a number of projects are either in progress or are at the planning stage. A major topic is the role played by photo-oxidants in atmospheric transformation processes. Many projects contribute to the international programme "Trophospheric Ozone Research" (TOR). TOR is part of the joint European research programme on technical and scientific advancement, which is called Eureka. Within Eureka, one of the subprogrammes, entitled Eurotrac, covers the distribution of airborne pollutants, among them trophospheric ozone.

Another important topic at present is NO_x compounds. Photo-oxidants and nitrogen oxides interact strongly in atmospheric transformation processes and the study of these processes is much emphasized.

There is some research activity on corrosion of materials. The area is not given top priority in Norway, however, because of intensive research in other countries.

NILU is responsible for the interpretation of the data from the air and precipitation monitoring programme as already discussed.

Acidification of soil and water

The mechanisms for acidification of soil and water are studied at field sites, in controlled experiments in the laboratory and even by manipulation experiments within real catchments. Understanding these mechanisms is of great importance for the evaluation of the effects of changes in acid deposition, the long-term harmful effects of deposition, and the upper limit with respect to tolerance to deposition for a certain area (critical load). Such knowledge is a necessary base when discussing optimum measures, for both emissions and various local countermeasures such as liming.

In Norway, we are lucky to have virtually pristine areas with respect to the long-range transport of air pollutants. These areas provide excellent sites for studying natural processes and for comparative surveys. In the Reversing Acidification In Norway (RAIN) project, advantage is taken of this (Wright, 1988; Wright et al., 1988).

By means of artificially applied acid and sampling of runoff water, the progress of acidification in a formerly pristine, but sensitive catchment, is studied (location 23, Fig. 1). The applied acid amounts to doses comparable to the acid loadings in the most heavily impacted areas in southernmost Norway on a yearly basis. Response and recovery of the runoff water quality are recorded after short exposures to acid addition, thereby simulating episodic events. One catchment is exposed to sulphuric acid, another to a mixture of nitric acid and sulphuric acid. The episodes have given a rapid runoff response for sulphate and serious aluminium surges. The nitrate contributes less to the acidification, presumably being absorbed by vegetation. The recovery time increased after every episode and the catchment is becoming permanently acidic. Reference catchments without acid additions are established at the same location.

Another, geologically similar, catchment (location 2, Fig. 1) in the southern-

most part of Norway has experienced acid loading for an extended period of time and has therefore become chronically acidic. An attempt to study the effects of reversing the acidification is being carried out there. Precipitation is collected by a roof which covers the entire catchment. The precipitated water is purified by ion exchange, sea salt is added and the water is then redeposited as natural clean precipitation. The recovery of the runoff water quality simulates what would happen if the acid loading were radically reduced. Calculations show that about 80% of the total acid deposition is excluded in this experiment. The remaining 20% occurs by dry deposition, which is still present beneath the roof.

Two reference catchments of similar size exist at the same location. One of these has the same equipment for collection of water, which is subjected to the same technical treatment, but without chemical treatment. The second reference catchment is without a roof and receives natural precipitation. The reference catchments thus serve as a control and are used to assess the effects of equipment and application techniques, which are found to be minor.

After 4 years of treatment, the sulphate in the runoff from the experimental catchment was halved. The nitrate level immediately approached zero. Labile aluminium has decreased to a level which may be non-harmful to fish. The pH, however, is improving only very slowly, indicating the role played by organic acid buffers.

Rain is conducted by NIVA, but a number of Norwegian and international scientists have been involved.

At another location, Høylandet (location 26, Fig. 1), situated in the middle of Norway where acid deposition is low, a reference site for interdisciplinary acid precipitation research has been established. One of the activities is the study of soil and stream chemistry. It provides the opportunity to evaluate theories and models with reference to a natural starting point believed to be similar to the conditions before the impact of pollutants (Christophersen et al. this volume, pp. 175-188).

A fairly extensive period of monitoring and research, as a result of our early concern about the acid rain problems in Norway, has provided a useful database for modelling work. Especially at NIVA, at the Center for Industrial Research (SI) and at the University of Oslo, groups are modelling runoff water quality. Computerized simulation models have proven to be powerful tools for interpretation of data-series and for analyzing complicated interactions between chemical, physical and biological processes which determine the resulting composition of stream water quality. Our knowledge about the key factors which have the main impact on the water quality will probably be greatly improved through modelling work. In addition, models are providing the means to predict the development, and to assess the effects, of changes in emissions of long-range transported air pollutants. They are therefore very valuable for the management of water resources and for supporting political negotiations.

The most widely known models developed by, or with contributions from,

Norwegian researchers are the Henriksen Model (Henriksen, 1980), the Birkenes Model (Christophersen et al., 1982; Stone and Seip, this volume, pp. 159–174) and the MAGIC Model (Cosby et al., 1985). They represent different approaches to the problem and are intended for different purposes. The Henriksen Model is empirical and is based on chemical status in a number of lakes receiving different acid loads. It is used for calculation of water chemistry for different scenarios of acid loads. The Birkenes Model is a conceptual, process oriented model aiming at understanding critical processes in acidification of catchments. Tentative predictions for various sulphur depositions have also been made. MAGIC is also a conceptual model, but is more suitable for regional-scale calculations and long-term predictions.

At present, the interaction between hydrology and chemistry, aluminium dynamics and speciation, sulphur mineralization and weathering are important areas for improvement within the modelling work (Stone and Seip, this volume, pp. 159–174). Nitrate is not yet included in the models mentioned, but certainly will be in the future. Organic acids should also be added, to improve surface water models.

Critical load is a useful concept for managers working on acid rain problems. Relevant results have come from different studies and a review work has been published on the determination of critical loads of acidic nitrogen and sulphur compounds for ecosystems typical of the Nordic countries (Nordic Council of Ministers, 1986). The project was undertaken by a group of experts from the Nordic countries. The main conclusions are that the critical load for sulphate (more precisely: strong acids with an anion which is mobile through soils) amounts to $10\text{--}20 \text{ keq km}^{-2} \text{ year}^{-1}$ over large areas and that the corresponding values for nitrogen in coniferous ecosystems are $10\text{--}20 \text{ kg N ha}^{-1}$. These figures may certainly need revision as knowledge about dose/effect relationships increases. Current depositions in southernmost Norway are approximately $50\text{--}100 \text{ keq km}^{-2} \text{ year}^{-1}$ of nitrogen.

Aluminium speciation and analyses are considered to be important factors when discussing the damaging effects of water acidification on aquatic biota. At NIVA, the University of Oslo and at the Norwegian University of Agriculture, aluminium chemistry is the focus of considerable research activity.

Aquatic fauna

There is no longer any doubt that the aquatic fauna in Norwegian freshwaters suffer from acidification. At present, one considers the possibility of recovery if sulphur emissions decrease further or as a response to local mitigating measures. This means that projects emphasizing the relationship between water quality and faunal status must be given priority. At the Høylandet site mentioned above, surveys are being carried out to obtain a total picture of the ecological balance in a pristine freshwater system. The results will serve as a reference when assessing damage in other, more or less impacted, areas. Such comparisons may give an indication of the tolerance of the surveyed species to water quality parameters.

The damage to fish is the most obvious effect of acidification in Norway so far. However, fish are very dependent on lower aquatic life. At the University of Bergen, a promising method based on samples of invertebrates has been developed, making it possible to classify the acidification status. The method is being implemented as a monitoring activity (see Monitoring, above).

Controlled experiments are also performed, especially with fish, to determine sensitivity to different components in water. Aluminium and calcium have been shown to have negative and positive effects, respectively, on aquatic organisms. Aluminium seems to be the critical toxic factor to aquatic biota and more important than the mere pH effect. High calcium concentrations counteract aluminium. Thus the effects of chemical substances depend on concentrations, as well as on the interrelationship between different components. For aluminium, the chemical species actually present are also very important (Rosseland et al., 1990).

Liming is the main countermeasure applied to Norwegian watercourses and lakes, although restocking of fish and stocking with more resistant species of fish is of some importance. The research activity is concentrated on evaluating the effectiveness of liming to reduce the cost and to identify optimum application techniques and liming constituents. Selection and breeding of resistant strains of trout may result in more successful restocking.

The Norwegian Institute for Environmental Research (NINA) has the main responsibility for freshwater biological research in Norway; however, NIVA and the Universities also have various activities in this area.

Forest and vegetation

Though an unambiguous connection between the long-range transport of air pollutants and damage to forests in Norway has not yet been shown, there exist indications that acidification and photo-oxidants contribute to stress, together with a number of other factors. The extensive damage to forests in Central Europe and the great economic interest in forestry were the main reasons for initiating the comprehensive research programme "Forest and Environment – Growth and Vigour" in 1986. The funds are granted from public sources in Norway and from EPRI (U.S.). The programme is chaired and mainly carried out by NISK.

The main difficulty in establishing the relationship between acid rain and forest health is the complicated interactions between a number of influencing factors and the complicated response from a complex ecosystem like a forest. The research programme investigates the relationship between vitality and growth on the one hand, and factors related to climate, soils, symbiotic organisms, pathogens and air pollution on the other. The health characteristics resulting from various stress factors may be demonstrated through comparative investigations between stands experiencing different environments, hopefully giving a better explanation of the possible cause/effect relationships involved.

One interesting result so far is related to tree growth at some experimental

sites which were irrigated with acidic water during the late seventies. The stands showed no reduced growth in the first years compared with controls; however, the growth was then significantly reduced and a minimum reached some years after the application was terminated. Recovery started 4–5 years after the termination of the treatment (Abrahamsen et al., 1987).

Other activities in this area are also, directly or indirectly, related to forest health. There are laboratory experiments at the University of Oslo in which trees of different age classes and species (mainly spruce) are exposed to various levels of SO₂ and ozone. Such controlled investigations are necessary for the interpretation of field results. At the same laboratory studies of oat and tobacco plants show damage at relatively low ozone concentrations (Myhre et al., 1988).

At the Høylandet reference site, soil and forest parameters are investigated and compared with the same parameters at a medium impacted area in southernmost Norway and a heavily impacted area in the Black Forest, W. Germany. When searching for a reference site, considerable effort was put into finding an area which is fairly typical of large areas of Norway, and even Europe, with respect to climate, ecosystems and geology. The data from Høylandet may therefore serve as an international reference, compensating to some extent for the lack of data from the pre-industrial period.

A number of studies on indicator organisms, such as lichens, mosses and other lower plants, which may respond more specifically than trees to stress factors, are being conducted at NINA and at the universities. There are also some surveys emphasizing the complete forest ecosystem, i.e. the total diversity of species. Such studies are dependent on a very precise surveying technique to reveal any relevant trend. One method, based on frequency of species within randomly selected 1 × 1 m grid elements, was developed at the University of Oslo and applied to an acidified site in southern Norway and a comparative study at Høylandet. The method (Økland, 1988) is also applied to monitoring of ground vegetation.

The results so far from Norwegian forest research give cause for concern about future forest damage. Oxidants, such as ozone, and soil acidification, which leads to leakage of nutrients from the soil, are suspected to be the most serious threats.

Metals

Concern about the effects of metals, transported by polluted air or released by soil acidification, is growing. Aluminium is especially important: it is a very common metal in soils and its hydroxides are an important buffer system when pH is < 5. Also, the levels of some toxic heavy metals, for example Pb, Cd and Hg, are suspected to have negative effects on wildlife and possibly on human health. Elevated levels of metals have been found in some species of birds and mammals and currently running projects are investigating possible damaging effects.

Two epidemiological surveys have shown a positive statistical correlation

between the incidence of presenile dementia and the levels of aluminium in natural water in areas in Norway (Vogt, 1986; Flaten, 1986). This should be interpreted merely as an indication of the possible interrelationship between acid loading and diseases. Health aspects are considered to be very important, however, and projects which hope to clarify these problems are continuing. Researchers at the Norwegian National Hospital, the University of Trondheim, the Central Bureau of Statistics and the National Institute of Public Health cooperate on such approaches.

Mosses are valuable indicators for assessing the deposited loads of metals. Because these plants take all their nutrients from air and precipitation, they reflect accumulated levels of deposited trace elements. The last year's shoots contain only metals taken up during that year; therefore, the deposition history may be traced back. This method has been used at the University of Trondheim and is implemented in monitoring programmes.

Metals are involved in many aspects of acid precipitation research and therefore form part of the studies at nearly all of the above-mentioned centers. In particular, a group at the University of Trondheim has contributed with a study on the distribution of, and effects from, metal pollutants (Steinnes, 1987). Berggren et al. (this volume, pp. 103-114) report on acidification of soils and some aspects of the dynamics of metals.

CONCLUSIONS

Acid precipitation is a very serious environmental problem. Serious damage has developed during the last 50-100 years, affecting freshwater life and probably vegetation and terrestrial fauna as well. Even human health may be influenced. Large economic losses are suspected due to increased corrosion of materials. Forestry and agriculture may suffer.

In Norway, awareness of the problems is very high and substantial resources are devoted both to document and to counteract to some extent the possible damages. Scientifically based knowledge is necessary for making the optimum decisions needed to resolve these problems. Hence acid precipitation monitoring and research are fairly large activities funded by public sources as well as by research institutions and universities.

The results so far show that the impact from long-range transported air pollutants is very extensive and still increasing. The depositions themselves have probably peaked, except for nitrogen compounds, but the deterioration of soils and waters seems to continue, the loads of acid components being well above critical levels in large areas of southernmost Norway. The delay in response is even more obvious within the biological systems. Ultimate effects may therefore include new areas as well as new species or ecosystems.

The priorities of Norwegian monitoring and research are decided from what are considered to be the most important topics in terms of extent of problems and lack of knowledge. Temporal trends of deposition of pollutants and of acidification of soils and waters, and the extension of damage to fish stocks and

forests are thus the main monitoring activities. Top priorities within research programmes are, at present, photo-oxidants, effects on forests, effects of aluminium, dose/response relationships for acidification of soils and waters and local measures to counteract loss of fish stocks.

Acid precipitation is an international problem, and the only real solution will require international cooperation on emission reductions. To reach international consensus on optimum measures, highly reliable scientific results are necessary. Hence, international cooperation in these aspects is also very valuable, enabling sound discussions and decisions. Norway cooperates in the international monitoring network and in major international research programmes, as well as in individual projects benefiting from joint efforts.

ACKNOWLEDGEMENTS

I very much appreciate the valuable comments and corrections to the manuscript given by my colleagues H.M. Seip and A. Stone.

REFERENCES

- Abrahamsen, G., B. Tveite, and A.O. Stuanes, 1987. Wet acid deposition effects on soil properties in relation to forest growth. Experimental results. In: D.P. Lavender (Ed.), Proc. IUFRO Workshop Woody Plant Growth in a Changing Physical and Chemical Environment, Vancouver, 27-31 July 1987, IUFRO, Vancouver, pp. 189-197.
- Christophersen, N., H.M. Seip, and R.F. Wright, 1982. A model for streamwater chemistry at Birkenes, Norway. *Water Resour. Res.*, 10: 977-996.
- Cosby, B.J., G.M. Hornberger, J.N. Galloway, and R.F. Wright, 1985. Modelling the effects of acid deposition: assessment of a lumped-parameter model of water and streamwater chemistry. *Water Resour. Res.*, 21: 51-63.
- Flaten, T.P., 1986. An investigation of the chemical composition of Norwegian drinking water and its possible relations with the epidemiology of some diseases. Thesis No. 51. Department of Chemistry University of Trondheim, Norway.
- Henriksen, A., 1980. Acidification of freshwaters - a large scale titration. In: D. Drabløs and A. Tollan (Eds), Proc. Int. Conf. Ecological Impact of Acid Precipitation. SNSF project, Oslo-Ås, Norway, pp. 68-74.
- Myhre, A., E. Forberg, H. Aarnes, and S. Nilsen, 1988. Reduction of net photosynthesis in oat (*Avena Sativa*) after treatment with low concentrations of ozone. *Environ. Pollut.*, 53: 265-271.
- Nordic Council of Ministers, 1986. Critical Loads for Nitrogen and Sulphur. Report 1986: 11, Environmental Protection Board of Sweden, P.O. Box 1302, 17125 Solna, Sweden.
- Økland, T., 1988. An ecological approach to the investigation of a beech forest in Vestfold, SE Norway. *Nord. J. Bot.*, 8: 375-407.
- Overrein, L.N., H.M. Seip, and A. Tollan, 1980. Acid precipitation: Effects on forest and fish. SNSF project report, FR 19/80, p. 175.
- Rosseland, B.O., T.D., Eldhuset, and M. Staurnes, 1990. Environmental effects of aluminium. Environmental effects of aluminium. *Environ. Geochem. Health*, in press.
- SFT, 1986. The Norwegian Monitoring Programme for Long-Range Transported Air Pollutants, Results 1980-1984. Report 230/86, The Norwegian State Pollution Control Authority (SFT), P.O. Box 8100, Dep., N-0032 Oslo 1, p. 95.
- SFT, 1987a. Overvåking av langtransportert forurensset luft og nedbør. Årsrapport 1986, Rapport 296/87. (The Norwegian Monitoring Programme for Long-Range Transported Air Pollutants. Annual report 1986, report 296/87.) The Norwegian State Pollution Control Authority (SFT), P.O. Box 8100, Dep., N-0032 Oslo 1.

- SFT, 1987b. 1000-Lake Survey 1986, Norway. Report 283/87. The Norwegian State Pollution Control Authority (SFT), P.O. Box 8100, Dep., N-0032 Oslo 1.
- SFT, 1988a. Overvåking av langtransportert forurenset luft og nedbør. Årsrapport 1987, Rapport 333/88. (The Norwegian Monitoring Programme for Long-Range Transported Air Pollutants. Annual report 1987, report 333/88.) The Norwegian State Pollution Control Authority (SFT), P.O. Box 8100, Dep., N-0032 Oslo 1.
- SFT, 1988b. 1000-Lake Fish Status Survey 1986, Norway. Report 314/88. The Norwegian State Pollution Control Authority (SFT), P.O. Box 8100, Dept., N-0032 Oslo 1.
- SFT, 1989. Overvåking av langtransportert forurenset luft og nedbør. Årsrapport 1988, Rapport 375/89. (The Norwegian Monitoring Programme for Long-Range Transported Air Pollutants. Annual report 1988, report 375/89.) The Norwegian State Pollution Control Authority (SFT), P.O. Box 8100, Dep., N-0032 Oslo 1.
- Steinnes, E., 1987. Impact of long-range atmospheric transport of heavy metals to the terrestrial environment in Norway. In: T.C. Hutchinson, and K.M. Meema, (Eds), Lead, Mercury, Cadmium and Arsenic in the Environment. SCOPE 1987. John Wiley, New York, pp. 107-117.
- Vogt, T., 1986. Vannkvalitet og helse. Analyse av en mulig sammenheng mellom aluminium i drikkevann og aldersdemens. (Water quality and health. Study of a possible relation between aluminium in drinking water and dementia.) Sosiale og Økonomiske Studier 61 (English abstract). Central Bureau of Statistics of Norway, Oslo.
- Wright, R.N., 1988. RAIN Project. Annual report for 1987. Acid Rain Research Report 16/1988. Norwegian Institute of Water Research, P.O. Box 33, Blindern N-0313 Oslo 3.
- Wright, R.F., E. Lotse, and A. Semb, 1988. Reversibility of acidification shown by whole-catchment experiments. *Nature*, 334: 670-675.



ACIDIFICATION IN NORWAY — LOSS OF FISH POPULATIONS AND THE 1000-LAKE SURVEY 1986

B.O. ROSSELAND and A. HENRIKSEN

Norwegian Institute for Water Research (NIVA), P.O. Box 69, Korsvoll, N-0808 Oslo 8 (Norway)

ABSTRACT

Several regional surveys have demonstrated that lakes and watersheds in widespread areas of southern Norway are affected by acidic precipitation. In autumn 1986, The Norwegian Institute for Water Research (NIVA) conducted the 1000-Lake Survey on behalf of the Norwegian State Pollution Control Authority (SFT).

The greatest loss of freshwater fish populations is to be found in the counties of Telemark, East and West Agder and Rogaland. The damage correlates well with pH and the concentrations of calcium and labile aluminium in the lakes. The number of barren lakes in Sørlandet and southern Vestlandet has doubled since 1971–75. The chemical changes are characterized by a decrease in calcium and sulphate and an increase in aluminium and nitrate. There has been little change in pH. The total land area affected by acidification damage has increased from 33 000 km² in 1974–79 to 36 000 km² in 1986. In 1986, over 18 000 km² were almost totally damaged compared with 13 000 km² in 1974–79, an increase in the most affected area of nearly 40%. The greatest increase was registered in eastern Norway.

Data from the 1000-Lake Survey indicated that 52% of the lakes in southern Norway were endangered. A 30% reduction in loadings of sulphur compounds would lead to the restoration of 28% of these lakes. A further reduction of 50% would ensure viable conditions for fish in 40% of the lakes, given a constant nitrate level in the lakes. The promising results from the RAIN project give optimism concerning the implementation of such prognoses.

INTRODUCTION

For decades, large areas of Europe and the eastern regions of North America have suffered from acid precipitation, resulting in acidification of waters, fish mortality and other ecological changes (Overrein et al., 1980). Acidic water has probably been the cause of fish mortality in Norway as far back as the turn of the century (Huitfeldt-Kaas, 1922), but it was only at the end of the 1950s that the link with acidic precipitation was established (Dannevig, 1959). Southernmost Norway and southwestern Norway receive the highest loadings of long-range transported air pollutants at the present time. These same areas are the most severely affected by fish mortality.

In Norway, regional surveys from 1974 to 1979 documented the occurrence of many acidic lakes in southern Norway (Wright and Snekvik, 1978; Sevaldrud et al., 1980). The acidification of lakes was associated with elevated concentra-

tions of sulphate, and a simple empirical relationship was developed to relate the pH of the lakes to sulphate deposition (Henriksen, 1979).

In 1980, the SNSF project ("Acid Precipitation — Effects on Forests and Fish", 1972–80) presented a status of fish populations in southern Norway, based on interviews over the period 1974–79 (Sevaldrud et al., 1980). Since 1980, developments have been followed by the National Programme for the Monitoring of Long-Range Transported Air Pollutants and Precipitation, which is coordinated by the State Pollution Control Authority (SFT).

In 1983, a revision of the fish status for lakes that still had a fish population in 1979 in the counties of Agder (southern Norway) showed that the loss of fish populations in areas affected by acidification was continuing (Rosseland et al., 1986; Sevaldrud and Skogheim, 1986). A survey of 1005 lakes located throughout Norway was conducted in 1986 ("The 1000-Lake Survey") to establish a baseline of chemical data and fish status prior to major planned reductions in emissions of acidic precursors in Europe. The survey was also designed to compare the present status of lakes with conditions in 1974/1975 (Henriksen et al., 1988, 1989).

This paper will summarize the results from surveys conducted in Norway, with special reference to the 1000-Lake Survey. For a better understanding of the correlation between lake chemistry and fish population status, some of the toxic mechanisms of acid waters will be described.

WHY FISH POPULATIONS DECLINE IN ACID WATERS

The loss of a fish population in an acid lake is the result of a long-term process. As the water chemistry changes and reflects the ongoing acidification of the catchment, different mechanisms in the fish will be affected. The hydrogen ion concentration (pH) and the concentration of the inorganic monomeric aluminium (Al) [often termed labile Al (LAl) or exchangeable Al] are the key factors in the toxicity of acid water (Baker and Schofield, 1980, 1982; Driscoll et al., 1980; Muniz and Leivestad, 1980; Driscoll, 1984; Rosseland and Skogheim, 1984). Nearly all levels in the physiology and behavior of fish are affected by low pH and high LAl concentration (Leivestad et al., 1987; Wood and McDonald, 1987; Neville and Campbell, 1988; Rosseland et al., 1990). Factors that ameliorate the toxicity of H^+ and Al at a given pH are a high concentration of calcium (Brown, 1983) and a high concentration of organics (humic matter or other chelating materials) (Baker and Schofield, 1980; Leivestad et al., 1987).

In Norway, the main mechanism leading to barren lakes is probably reproduction failure due to a high mortality of eggs and alevins (Jensen and Snekvik, 1972; Rosseland et al., 1980; Rosseland, 1986). Over a long time period, often 10–20 years, the population ages with no or few recruits, until all the fish are gone.

Most salmonids in Norway spawn in running waters. The spawning period in autumn often coincides with heavy rain storms, resulting in low pH of

runoff. The high mortality of spawners and post spawners observed in some areas might thus be explained by such episodes in conjunction with marginal winter and spring conditions (Leivestad and Muniz, 1976; Rosseland et al., 1980; Frenette and Dodson, 1984; Henriksen et al., 1984; Skogheim et al., 1984; Rosseland, 1986). Fish populations that experience losses of old fish (juvenilization) and reproduction failure (ageing) might thus vanish rapidly, often within less than 10 years.

In Norway, most lakes are privately owned, and the fish have been important for consumption and recreation. Changes in catch or quality of the fish are therefore rapidly noticed by the owners. Information given by the lake owners correlates well with results from test-fishing programs (Rosseland et al., 1980). The interview method used in the Norwegian surveys (Wright and Snekvik, 1978; Sevaldrud et al., 1980; Sevaldrud and Skogheim, 1986; Henriksen et al., 1989) gives a good but conservative estimate of the situation in Norwegian lakes.

METHODS USED IN REGIONAL SURVEYS

The major regional surveys in Norway have included collection of data for both water chemistry and fishery status of the lakes. Water samples were collected from the outlets of the lakes, in most cases within a short time period in the autumn. Information about fish populations was recorded by the use of questionnaires and help from the lake owners, county environmental authorities, or other persons with first-hand information about the lakes. For the 1000-Lake Survey in 1986, the lakes were selected on the basis of their location in areas of bedrock expected to give poorly-buffered runoff water (granite, gneiss and migmatite). Most of the lakes were larger than 0.2 km², located at a high altitude in watersheds, and not subject to any significant water regulation or local sources of pollution.

Approximately 40 species of freshwater fish, including eel, have been registered in Norwegian watersheds. In the lakes surveyed, brown trout (*Salmo trutta* L.) and perch (*Perca fluviatilis* L.) are the dominant species in eastern and southernmost Norway, while arctic char (*Salvelinus alpinus* L.) and brown trout dominate southwestern Norway and further north (Henriksen et al., 1989).

CHANGES AND STATUS OF FISH POPULATIONS

Sevaldrud et al. (1980) reported on the status of > 2600 populations of brown trout, showing a loss up to 1979 of > 50%, the losses being particularly rapid after 1960. An area of 33 000 km² was affected. In 13 000 km² of this area the fish populations were virtually extinct. Based on these data, they predicted a total loss of 80% in the most affected counties (Rogaland, Vest-Agder, Aust-Agder and Telemark) by the next decade (Sevaldrud et al., 1980).

In 1983, > 600 lakes from the counties of Vest-Agder and Aust-Agder that had a fish population in 1978 were resampled (Sevaldrud and Skogheim, 1986).

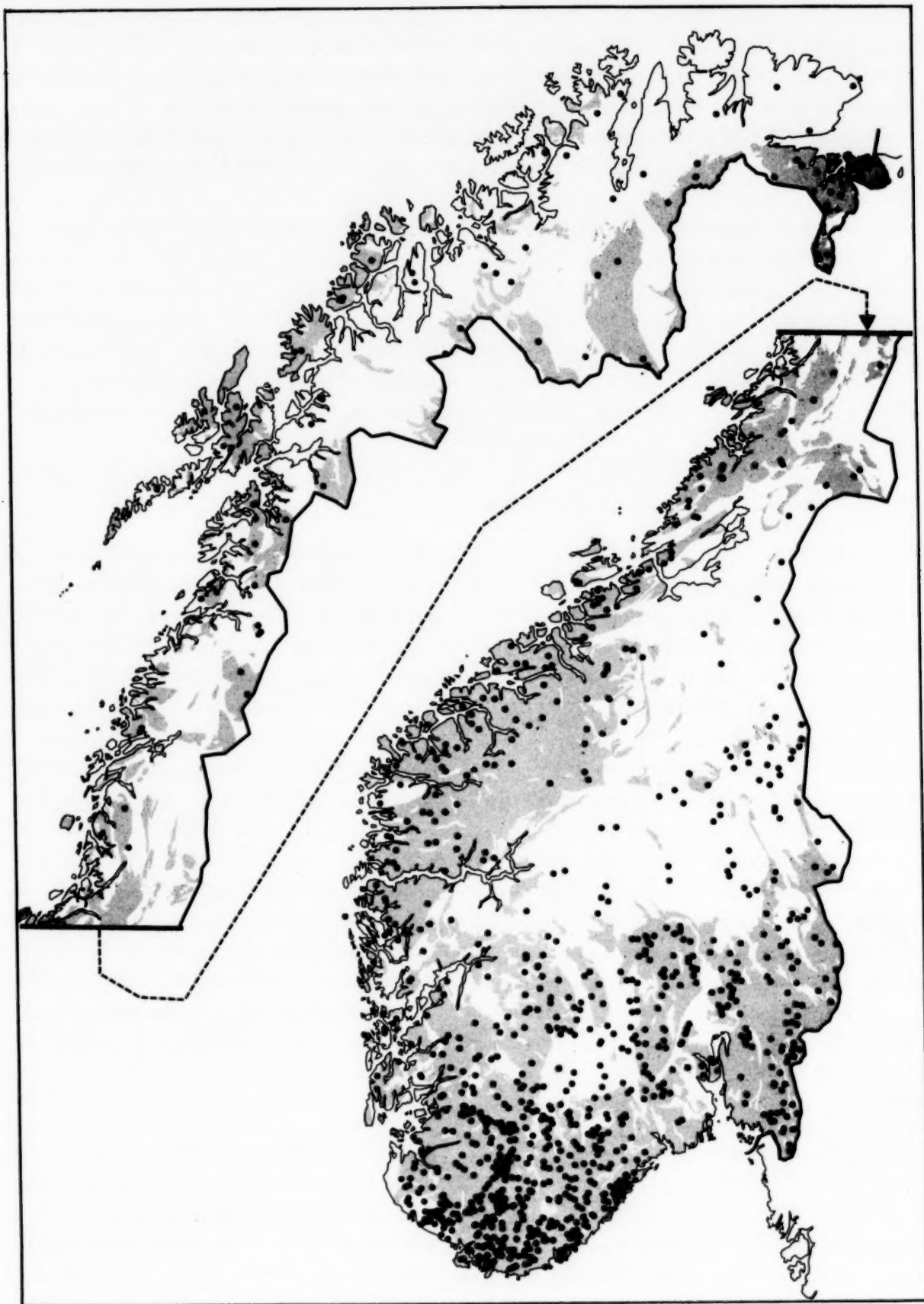


Fig. 1. The 1000-Lake Survey 1986. Location of the 1005 lakes sampled in Norway during fall 1986. Bedrock expected to produce poorly buffered runoff water (granite, gneiss, migmatite) is shown in grey (after Henriksen et al., 1988).

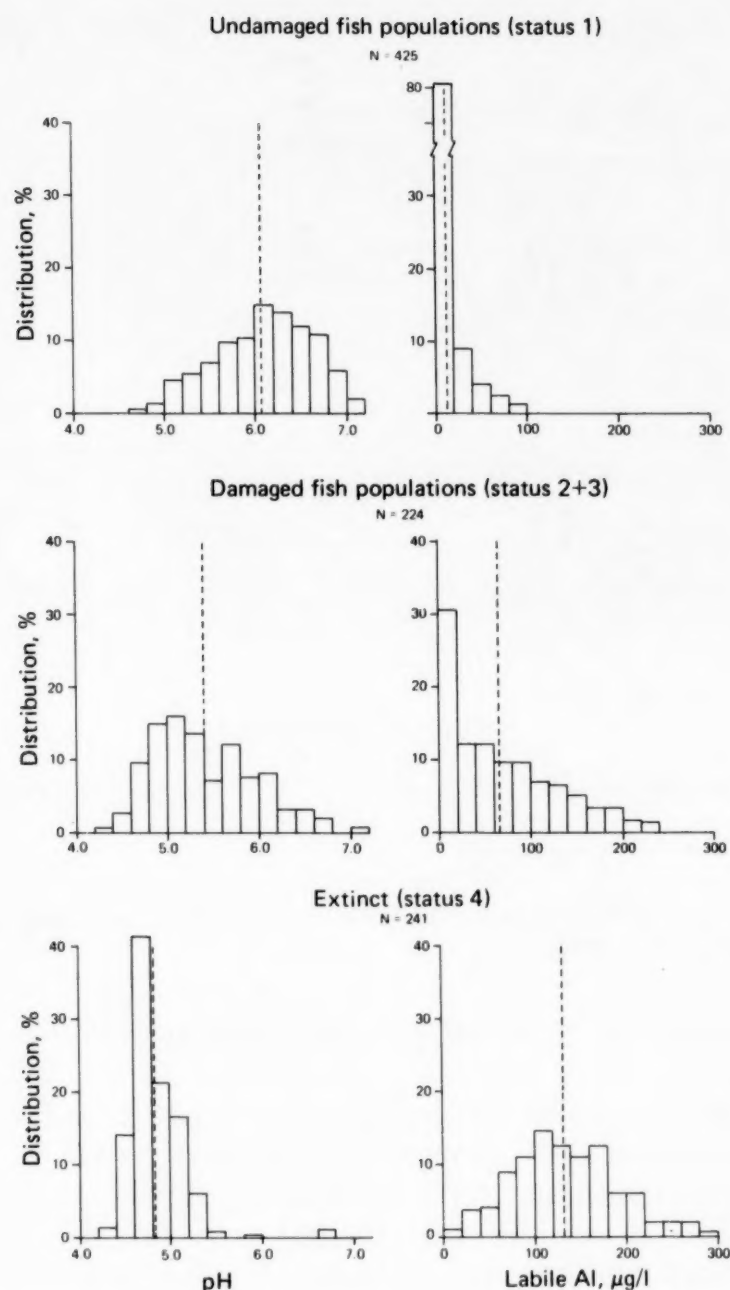


Fig. 2. The 1000-Lake Survey 1986. The distribution of pH and labile aluminium ($\mu\text{g l}^{-1}$) in lakes with varying fish status. The dashed line represents the mean value for all lakes in each group (after Henriksen et al., 1989).

During the period 1978–1983, 30% of the remaining brown trout populations and 12% of the perch population were lost, resulting in a total loss in the area of 71% of the brown trout and 43% of the perch populations. This trend correlated well with the general impression from Scandinavia that the damage to fish populations was continuing (Rosseland et al., 1986).

In the 1000-Lake Survey, water samples from 1005 lakes and fish status data from 891 of these were collected (Fig. 1, Henriksen et al., 1988, 1989).

Stress to fish populations correlates well with the pH and concentrations of labile aluminium and calcium in damaged and barren lakes. pH is generally

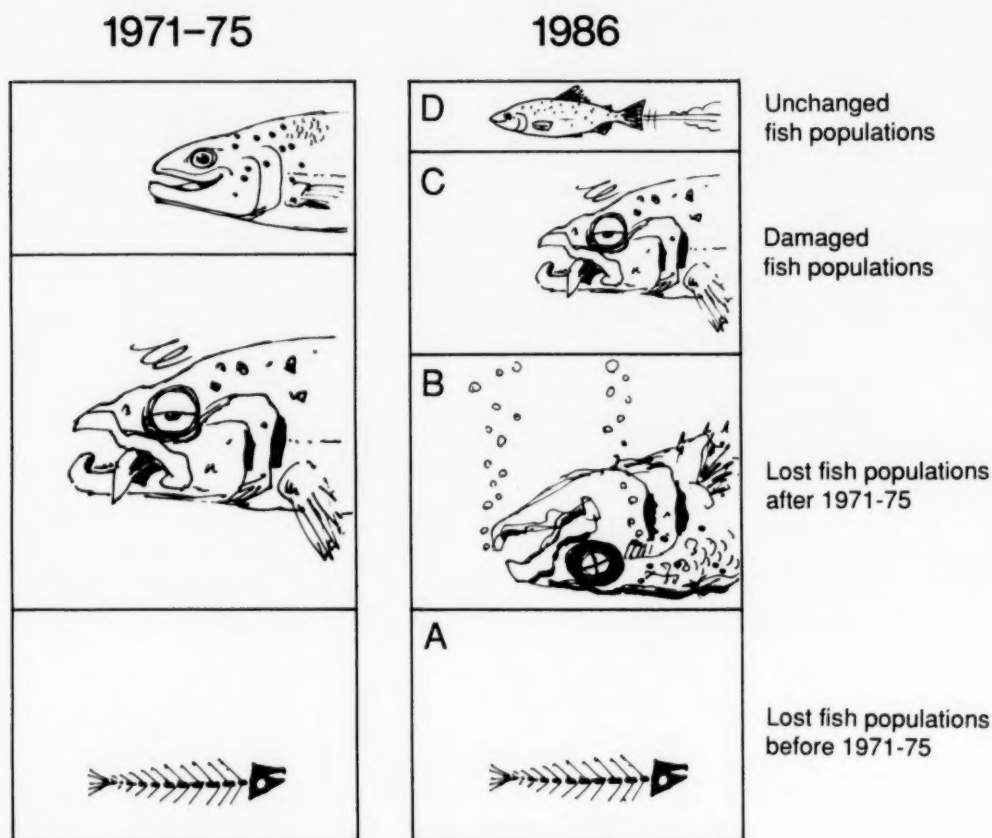


Fig. 3. The 1000-Lake Survey 1986. Changes in fish status for 254 lakes in southern Norway from 1971-75 to 1986 (adapted from Henriksen et al., 1989).

low, labile aluminium concentrations are high, and calcium concentrations are low.

The distribution of pH values and concentrations of labile aluminium for lakes in the fish status categories undamaged, damaged and extinct, is given in Fig. 2. Lakes with an unaffected fish population have the highest pH values and the lowest concentrations of labile aluminium, with the pH exceeding 5.0 in 97% of these lakes. In lakes where populations are damaged, pH values are scattered, but there is a predominance (64%) of lakes with pH < 5.6, i.e. lakes without bicarbonate buffering capacity. The concentrations of aluminium in the lakes also vary widely, with 55% < $60 \mu\text{g l}^{-1}$.

In lakes with pH in the range 4.6-4.8, the calcium content is 40% higher and the aluminium content ~15% lower in damaged lakes compared with barren lakes. When the pH is in the range 4.8-5.0, the corresponding figures are 40 and 30%, respectively. This clearly emphasizes the significance of calcium and aluminium for fish survival. In lakes of the same pH, the lakes that still have fish have a higher calcium level and a lower aluminium level than barren lakes. Of 117 perch lakes of pH < 5.5, there is a clear trend indicating that perch survive at a lower pH when the TOC level (total organic carbon) is high. Perch survived in lakes having a pH 0.5 units lower, when TOC increased from 2 to 6 mg TOC l^{-1} .

1000 LAKE FISH STATUS SURVEY 1986 NORWAY

The Norwegian State Pollution Control Authority – SFT.
Norwegian Institute for Water Research – NIVA.

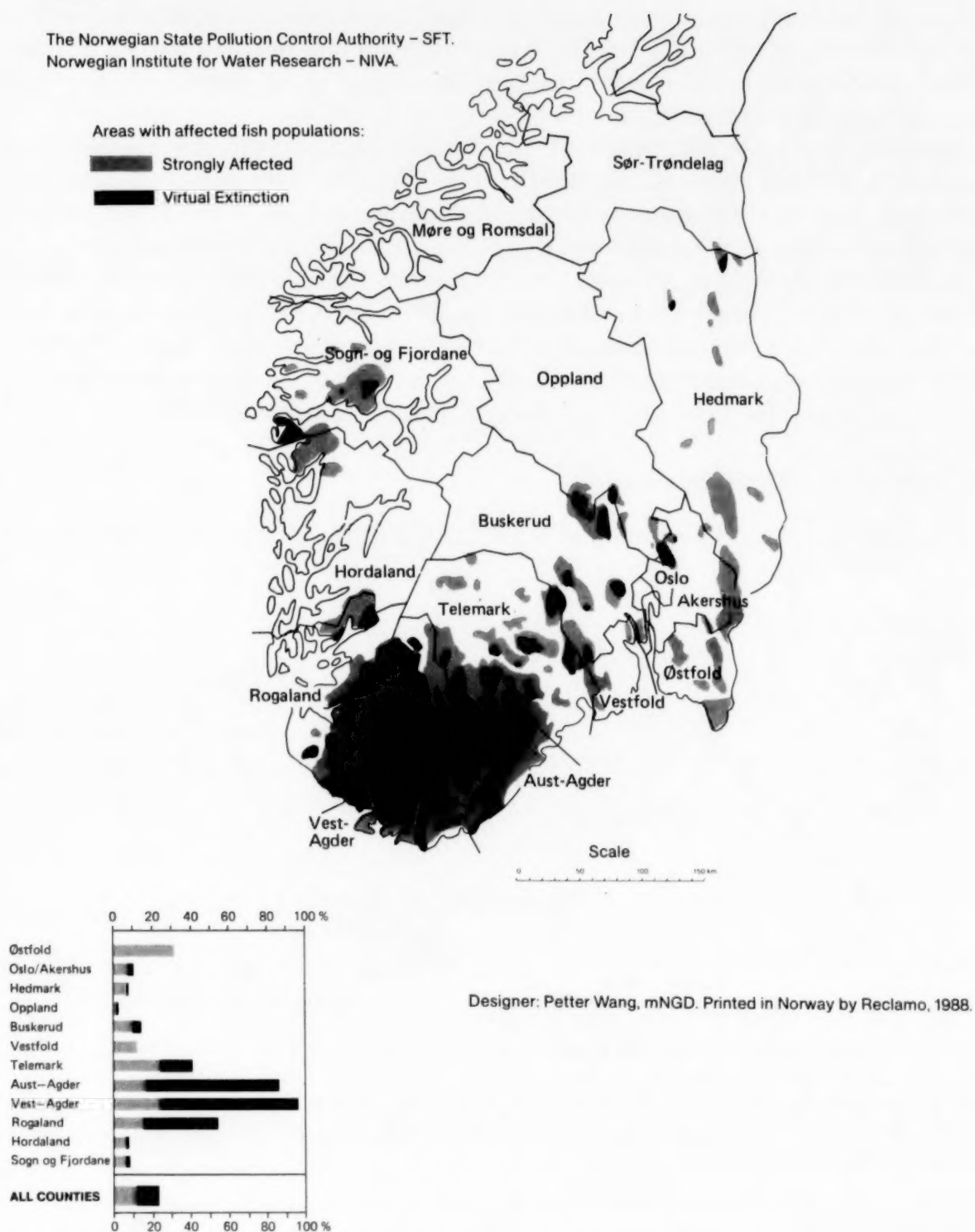


Fig. 4. The 1000-Lake Survey 1986. Areas in southern Norway in which fish populations are affected by acidification. This map is an updated version of the SNSF map from 1974–79. Revisions are based on information from Annual Reports 1980–1987 from the Norwegian State Pollution Control Authority and from the 1000-Lake Survey. The relative sizes of affected areas within each county are shown in the bar diagram (after Henriksen et al., 1989).

Of the lakes with fish status, there was available information for 245 of these lakes from the period 1971–75. These lakes are situated in the southernmost and most affected areas of Norway. In 1971–75, 30% of these lakes were barren, 47% had one or more reduced fish populations, while there was no registration, as yet, of changes in the fish populations in 23% of the lakes. By 1986 the number of barren lakes had risen to 64% (Fig. 3A, B), while only 10% of the lakes surveyed had fish populations which had not been harmed by acidic water (Fig. 3D). Thus, 48% of the lakes having fish in 1971–75 had become barren by 1986. These results confirm the predictions of Sevaldrud et al. (1980) and the data from Sevaldrud and Skogheim (1986).

Based on available information from monitoring programs and the previous surveys, a revised map of the acidified areas with fish damaged has been produced (Fig. 4, Henriksen et al., 1989). Comparison with the SNSF survey (Sevaldrud et al., 1980) shows that regions affected have increased by ~9%, from 33 000 to 36 000 km² in area. In 1986, more than 18 000 km² were almost totally damaged in contrast to 13 000 km² in 1974–1979, an increase of 38%. The regions affected cover an area of 22% of the counties of southern Norway. These counties constitute approximately half of Norway's total area so that, in all, 11% of the total land area is affected (Henriksen et al., 1989).

CHANGES IN WATER CHEMISTRY

The 1000-Lake Survey demonstrated that ~70% of the lakes sampled in

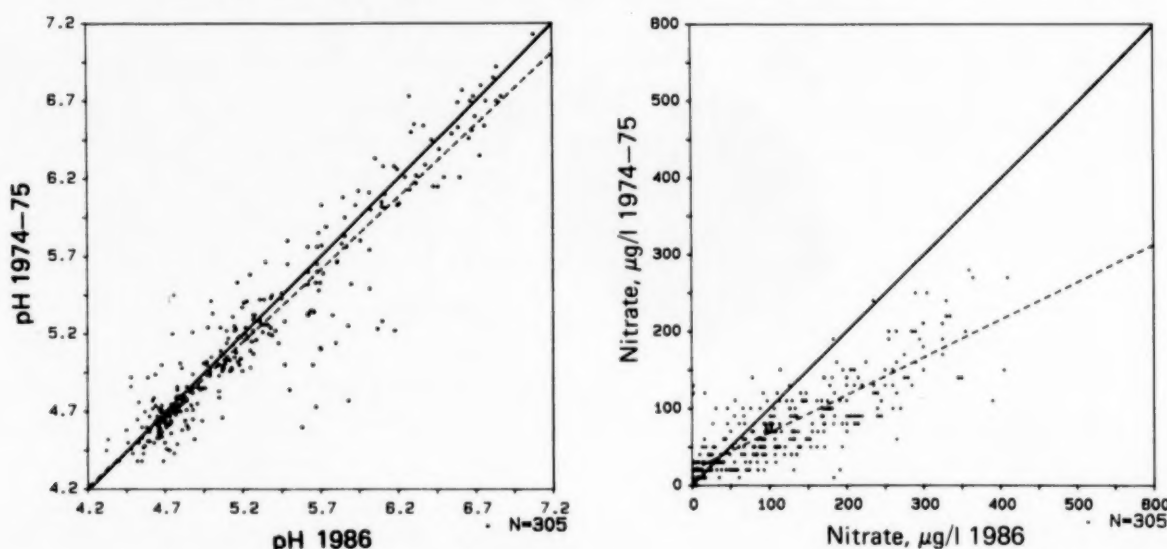


Fig. 5. The 1000-Lake Survey 1986. pH values in 1986 in comparison with those in 1974–75 for 305 lakes in southern Norway. Regression line is $y = 0.3 + 0.93x$ ($r = 0.94$). Lakes that fall within a zone of ± 0.05 pH units from the 1:1 line have not changed in pH. Lakes that fall below or above the zone are considered to have higher or lower pH, respectively, in 1986 than in 1974–75 (after Henriksen et al., 1988).

Fig. 6. The 1000-Lake Survey 1986. Nitrate values in 1986 in comparison with conditions in 1974–75 for 305 lakes in southern Norway. Regression line is $y = 20 + 0.49x$ ($r = 0.75$). Lakes that fall within a zone of $\pm 10 \mu\text{g NO}_3 \text{ l}^{-1}$ from the 1:1 line have not changed. Lakes that fall above or below the zone have lower or higher concentrations, respectively, in 1986 than in 1974–75 (after Henriksen et al., 1988).

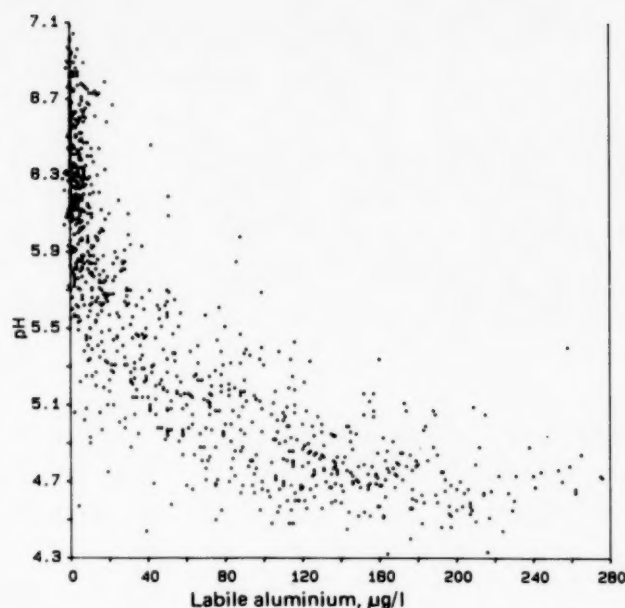


Fig. 7. The 1000-Lake Survey 1986. pH and labile aluminium are strongly correlated in 1005 lakes in Norway (after Henriksen et al., 1989).

southernmost Norway have lost their bicarbonate buffering capacity ($\text{pH} < 5.0$). Comparing data from 1974–75 with that from 1986, the pH of the 305 lakes sampled in both periods had changed little (Fig. 5), in spite of a reduction in sulphate concentration in the most affected lakes. In most of the lakes in Sørlandet, however, the nitrate concentrations have doubled from 1974–75 to 1986 (Fig. 6) (Henriksen et al., 1988). Little change was found in lakes in western and interior parts of southern Norway. Lakes in eastern Finmark (northern Norway) are also greatly affected by acid rain (being close to large emissions in the U.S.S.R).

More than 70% of the lakes had concentrations of non-marine calcium and magnesium of $< 75 \mu\text{eq l}^{-1}$; half of them had a calcium concentration of $0.4\text{--}0.5 \text{ mg Ca l}^{-1}$. Sixty percent of the lakes had a TOC of $< 2 \text{ mg C l}^{-1}$. There was a very strong correlation between pH and labile aluminium in the lakes (Fig. 7), and the concentration of aluminium had increased in the most affected lakes from 1974–75 to 1986 (Henriksen et al., 1989). In these same lakes, the concentration of calcium and magnesium had decreased, resulting in more unfavourable conditions for fish. These chemical changes can thus, at least partly, explain the changes in fish status over the same time period.

REDUCTION IN DEPOSITION — EFFECTS ON FISH?

To estimate whether a 30% reduction in sulphate emission, agreed by many countries by 1993, will have any effect on fishery status in Norway, an empirical model was used (Henriksen et al., 1988). Using the data from 885 lakes from the 1000-Lake Survey, the 462 lakes having fish problems will experience a restoration, after a 30, 50 and 70% reduction in sulphate depositions, of approximately 28, 40 and 60%, respectively (Henriksen et al., 1989, Fig. 8).

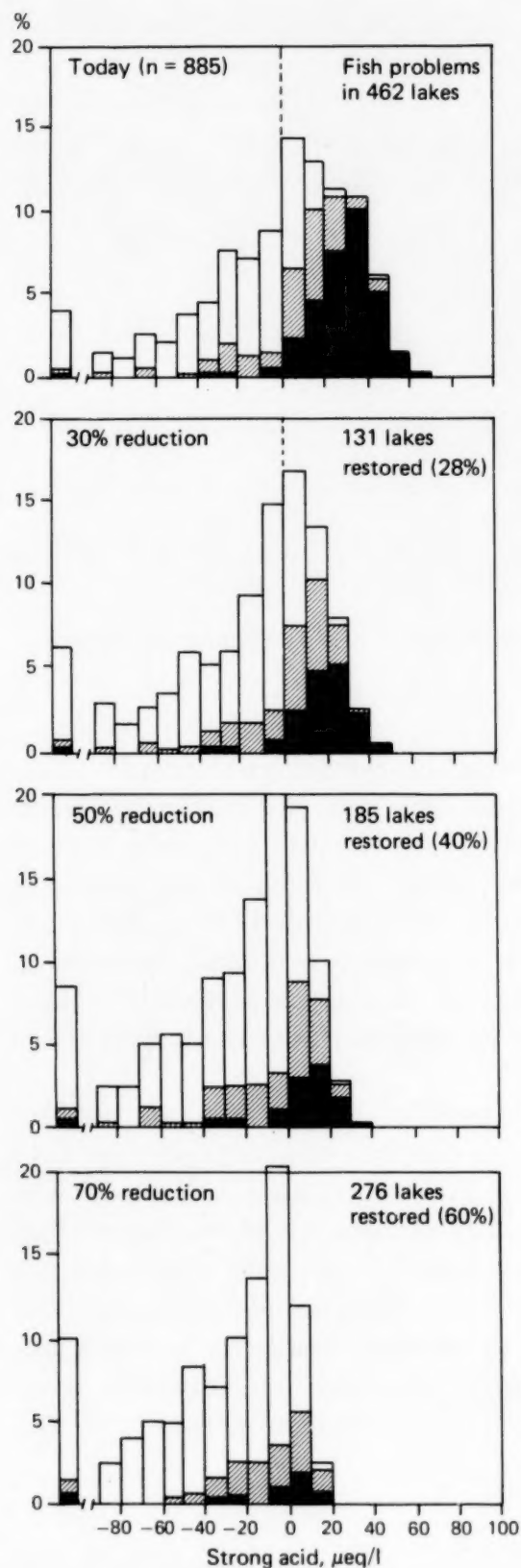


Fig. 8. The 1000-Lake Survey 1986. The frequency distribution for content of strong acid and fish status for 885 lakes in 1986, calculated on the basis of a 30, 50 and 70% reduction in the lakes' sulphate concentrations. Lakes which are barren, or with at least one lost population, are shown in black; lakes with at least one damaged population are shaded; and undamaged lakes are unshaded (after Henriksen et al., 1989).

These results are based on conservative estimates, but are strongly dependent on no further increases in nitrate in runoff to the lakes and streams. Based on the promising results from the RAIN project ("Reversing Acidification in Norway", Wright et al., 1988; see also Taugbøl, this volume, pp. 23-43), no delays in efforts to reduce acidic depositions should be tolerated.

REFERENCES

- Baker, J.P., and C.L. Schofield, 1980. Aluminium toxicity to fish as related to acid precipitation and Adirondack surface water quality. In: D. Drabløs, and A. Tollan, (Eds), Ecological Impact of Acid Precipitation. SNSF project, Oslo-Ås, Norway, pp. 292-293.
- Baker, J.P. and C.L. Schofield, 1982. Aluminium toxicity to fish in acidic waters. *Water, Air Soil Pollut.*, 18: 289-309.
- Brown, D.J.A., 1983. Effects of calcium and aluminium concentration on the survival of brown trout (*Salmo trutta*) at low pH. *Bull. Environ. Contam. Toxicol.*, 30: 382-387.
- Dannevig, A., 1959. Nedbørens innflytelse på vassdragenes surhet og på fiskebestanden (Influence of precipitation on river acidity and fish population). *Jeger og fisker*, 3: 116-118 (in Norwegian).
- Driscoll, C.T., 1984. A procedure for the fractionation of aqueous aluminium in dilute acidic waters. *Int. J. Environ. Anal. Chem.*, 16: 267-283.
- Driscoll, C.T., J.P. Baker, J.J. Bisogni, Jr. and C.L. Schofield, 1980. Effects of aluminium speciation on fish in dilute acidified waters. *Nature*, 284: 161-164.
- Frenette, J.-J. and J.J. Dodson, 1984. Brook trout (*Salvelinus fontinalis*) population structure in acidified Lac Tantaré, Quebec. *Can. J. Fish. Aquat. Sci.*, 41: 865-877.
- Henriksen, A., 1979. A simple approach for identifying and measuring acidification of freshwater. *Nature*, 278: 542-545.
- Henriksen, A., O.K. Skogheim, and B.O. Rosseland, 1984. Episodic changes in pH and aluminium-speciation kill fish in a Norwegian salmon river. *Vatten*, 40: 225-260.
- Henriksen, A., L. Lien, T.S. Traaen, I.S. Sevaldrud, and D.F. Brakke, 1988. Lake Acidification in Norway — present and predicted chemical status. *Ambio*, 17: 259-266.
- Henriksen, A., L. Lien, B.O. Rosseland, T. Traaen, and I.S. Sevaldrud, 1989. Lake acidification in Norway. Present and predicted fish status, *Ambio*, 18: 314-321.
- Huitfeldt-Kaas, H., 1922. Om aarsaken til massedød av laks og ørret i Frafjordelven, Helleelven og Dirdalselven i Ryfylke høsten 1920 (On the cause of mass death of salmon and trout in the River Frafjord, River Helle and River Dirdal in Ryfylke, autumn 1920). *Nor. Jæger- Fiskefor. Tidsskr.*, 37-44 (in Norwegian).
- Jensen, K.W. and E. Snekvik, 1972. Low pH levels wipe out salmon and trout populations in southern Norway. *Ambio*, 1: 223-225.
- Leivestad, H. and I.P. Muniz, 1976. Fish kill at low pH in a Norwegian river. *Nature*, 259: 391-392.
- Leivestad, H., E. Jensen, H. Kjartansson, and L. Xingfu, 1987. Aqueous speciation of aluminium and toxic effects on Atlantic salmon. *Ann. Soc. R. Zool. Belg.*, 117(Suppl. 1): 387-398.
- Muniz, I.P. and H. Leivestad, 1980. Toxic effects of aluminium on the brown trout (*Salmo trutta* L.). In: D. Drabløs, and A. Tollan, (Eds), Ecological Impact of Acid Precipitation. SNSF project, Oslo-Ås, Norway, pp. 320-321.
- Neville, C.M. and P.G.C. Campbell, 1988. Possible mechanisms of aluminum toxicity in a dilute, acidic environment to fingerlings and older life stages of salmonids. *Water, Air Soil Pollut.*, 42: 311-327.
- Overrein, L., H.M. Seip, and A. Tollan, 1980. Acid precipitation — effects on forest and fish. Final report of the SNSF project 1971-1980. SNSF project, Nisk, N-1432 AÅ, FR 19/80, p. 175.
- Rosseland, B.O., 1986. Ecological effects of acidification on tertiary consumers. Fish Population responses. *Water, Air Soil Pollut.*, 30: 451-460.
- Rosseland, B.O. and O.K. Skogheim, 1984. A comparative study on salmonid fish species in acid aluminium-rich water. II. Physiological stress and mortality of one and two year old fish. *Rep. Inst. Freshwater Res., Drottningholm*, 61: 186-194.

- Rosseland, B.O., I.H. Sevaldrud, D. Svalastog and I.P. Muniz, 1980. Studies of freshwater fish population — effects of acidification on reproduction, population structure, growth and food selection. In: D. Drabløs and A. Tollan (Eds), Ecological Impact of Acid Precipitation. SNSF project, Oslo-Ås, Norway, pp. 336–337.
- Rosseland, B.O., O.K. Skogheim, and I.H. Sevaldrud, 1986. Acid deposition and effect in Nordic Europe. Damage to fish populations continue to apace. *Water, Air Soil Pollut.*, 30: 65–74.
- Rosseland, B.O., T.D. Eldhuset, and M. Staurnes, 1990. Environmental effects of aluminium. *Environ. Geochem. Health* (in press).
- Sevaldrud, I.H. and O.K. Skogheim, 1986. Changes in fish populations in southernmost Norway during the last decade. *Water, Air Soil Pollut.*, 30: 381–386.
- Sevaldrud, I.H., I.P. Muniz, and S. Kalvenes, 1980. Loss of fish populations in southern Norway. Dynamics and magnitude of the problem. In: D. Drabløs, and a. Tollan, (Eds), Ecological Impact of Acid Precipitation. SNSF project, Nisk, N-1430 Ås, pp. 350–351.
- Skogheim, O.K., B.O. Rosseland, and I.H. Sevaldrud, 1984. Deaths of spawners of Atlantic salmon in Rivere Ognå, SW Norway, caused by acidified aluminium-rich water. *Rep. Inst. Freshwater Res.*, Drottningholm, 61: 195–202.
- Wood, C.M. and D. McDonald, 1987. The physiology of acid/aluminium stress in trout. *Ann. Soc. R. Zool. Belg.*, 117(Suppl. 1): 399–410.
- Wright, R.F. and E. Snekvik, 1978. Acid precipitation: chemistry and fish populations in 800 lakes in southernmost Norway. *Verh. Int. Verein. Limnol.*, 20: 765–775.
- Wright, R.F., E. Lofse, and A. Semb, 1988. Reversibility of acidification shown by whole-catchment experiments. *Nature*, 334: 670–675.

ACID PRECIPITATION: BIOLOGICAL MONITORING OF STREAMS AND LAKES

ARNE FJELLHEIM and GUNNAR G. RADDUM

Department of Animal Ecology, Museum of Zoology, University of Bergen, N-5007 Bergen (Norway)

ABSTRACT

This article summarizes the activities and results from the Norwegian invertebrate acidification monitoring program. The program was started in 1981 and includes at present five watersheds. A key tool in the invertebrate monitoring program is a model which calculates an acidification index based on acid-sensitive invertebrates. The model is briefly presented, together with the acidification tolerance limits for different invertebrates. The degree of damage due to acidification differed both between watersheds and over time. Generally, the watersheds in the southernmost parts of Norway were most acidified. In watersheds on the west coast, maximum acidification was measured in 1983–1984. This was correlated with episodic kills of young Atlantic salmon. During recent years, acidification has decreased in most rivers with the exception of those found in the southernmost regions. The rivers are, however, still vulnerable due to poor buffer capacity.

INTRODUCTION

Acidification of freshwater ecosystems is recognized as a major environmental problem in many parts of the world (Haines, 1981). In Norway, Atlantic salmon (*Salmo salar* L.) was the first species of fish affected by acid deposition (Huitfeldt-Kaas, 1922; Dahl, 1927; Jensen and Snekvik, 1972). Many rivers which today have lost their salmon populations, were formerly excellent rivers for sports fishing. In 1883, a total rod catch of 86 tons of salmon was recorded for 10 of these rivers (Hesthagen and Mejdell Larsen, 1987). In addition, populations of brown trout (*Salmo trutta* L.) are seriously affected in southernmost Norway, the extinction rate being especially high since about 1960 (Muniz et al., 1984).

Most of the present knowledge concerning the effect of acidification on streams in Norway was documented during the joint project "Acid Precipitation — Effects on Forests and Fish", which was published in 1980 (Overrein et al., 1980). This project formed a basis for later acidification studies. In 1980, a monitoring program which included chemical assessment of airborne pollution on river catchments as well as studies on fish, was begun. Invertebrate monitoring was included in this program in 1981.

A large amount of environmental data on invertebrates accumulated during these projects. Together with experimental data, this formed the basis for a



Fig. 1. Map of South Norway showing the geographical location of the watersheds.

model which calculates numerical acidification values for a site or watershed (Raddum and Fjellheim, 1985; Raddum et al., 1988). This model has been a key tool both in mapping the degree of acidification damage and investigating the intensity of acidification, based on biological monitoring during the 1980s.

This paper gives a brief description of the model, summarizes the activities of the invertebrate monitoring program and gives results for the variations in acidity based upon distribution of acid-sensitive organisms.

STUDY AREAS

The geographical location of the study areas is shown in Fig. 1. The monitoring program was started in 1981 in two small watersheds near Farsund, southern Norway. In the period 1982–1984, four other watersheds were added to the program. All catchments are situated in southern and western Norway in regions with high precipitation and with bedrock sensitive to acidification (Muniz and Leivestad, 1980; Overrein et al., 1980; Henriksen, 1985). This is also reflected in the water quality, which is generally soft.

Farsund

Two small adjoining watersheds near Farsund were included in the monitoring program in 1981. The watersheds (total catchment area 6 km²) are part of a region which is highly acidified (Muniz and Leivestad, 1980). Both watersheds are populated by brown trout. Test fishing in a small lake, L. Saudlandsvatn, has shown a strong population decrease. In 1977, this lake had a dense population of stunted trout. During the 1980s, recruitment failure was

documented and, in 1987, spawning took place only in the outlet brook (State Pollution Control Authority, 1988). Chemical monitoring of the lake shows that both the inlets and outlets are chronically acid ($\text{pH} < 5.0$) during long periods in the winter and spring (Jonsson and Blakar, 1987).

Ogna

The catchment area of the River Ogna (112 km^2) consists of two main basins. One of them, the River Helgaa, which runs into the River Ogna a few hundred meters from the sea, is highly acidified. Water from this catchment is used in a hydroelectric power plant situated 3 km from the sea on the main river. Acid water from this power plant (pH , 4.7; labile Al, $360 \mu\text{g l}^{-1}$) has caused mortalities in spawning Atlantic salmon in the downstream river (Hesthagen et al., 1982; Skogheim et al., 1984). Also, the death of young salmon and brown trout has occasionally been reported in this part of the river.

Vikedal

The River Vikedal (119 km^2), which has been monitored since 1982, is characterized by a highly episodic acidification pattern. In the main river, fish death (mainly salmon parr) has been documented each spring during 1981–1986 (Hesthagen and Mejdell Larsen, 1987). The highest mortality was observed in 1984 (172 salmon, 31 trout). In later years, mortality has been less serious (Hesthagen, 1986; Hesthagen and Mejdell Larsen, 1987). The acid episodes in the River Vikedal are characterized by rapid decreases in pH accompanied by increased concentrations of labile aluminum (Henriksen et al., 1987). These episodes coincide with increased water levels and decreased calcium concentrations. Since 1987, acidification in the lowermost 10 km of the river has been mitigated by liming snowmelt and spring spates.

Gaular

The River Gaular (630 km^2) is situated in western Norway. The geology of the catchment area, and especially the upper regions, gives a low buffer capacity. This is most evident in the southern mountain area. Since 1947, several cases of fish kill have been documented. This mainly affected populations of resident brown trout.

A survey in 1984 showed that two lakes had lost their trout populations, while more than 50% of the populations were reduced (Lien, 1986). The lowland part of the river is, however, well buffered and no harmful effects of acidification have been observed in the salmon population.

Nausta

The River Nausta (274 km^2) is the northernmost of the monitored rivers. The

bedrock of the catchment area is mainly composed of slow weathering rocks, making the river water sensitive to acid deposition. In contrast to the River Gaular, the Atlantic salmon population has also been affected. This was especially evident in the beginning of the 1980s (Raddum et al., 1988). The damages have been mitigated by a stocking program.

METHODS

Benthic samples are collected twice a year from a selected number of localities in each watershed (Fig. 1). Sampling was carried out according to the method of Frost et al. (1971) using a collecting net of 250 μm . The samples were preserved in ethanol and later sorted and identified in the laboratory. In addition to benthic samples, stomach contents of Atlantic salmon and trout have been investigated.

In addition to the yearly monitoring, a more intensive invertebrate sampling program has been carried out at longer time intervals. These studies consist of up to 50 samplings from lotic and lentic localities and give information on the acidification levels in larger parts of the watershed.

After identification, each benthic sample is given an acidification index according to the method described by Raddum and Fjellheim (1985) and Raddum et al. (1988).

Figure 2 gives an example of how the model is used. Invertebrates are divided into four categories according to sensitivity to acidification:

- (a) species becoming extinct at pH < 5.5
- (b) species becoming extinct at pH < 5.0
- (c) species becoming extinct at pH < 4.7
- (d) species tolerating pH < 4.7.

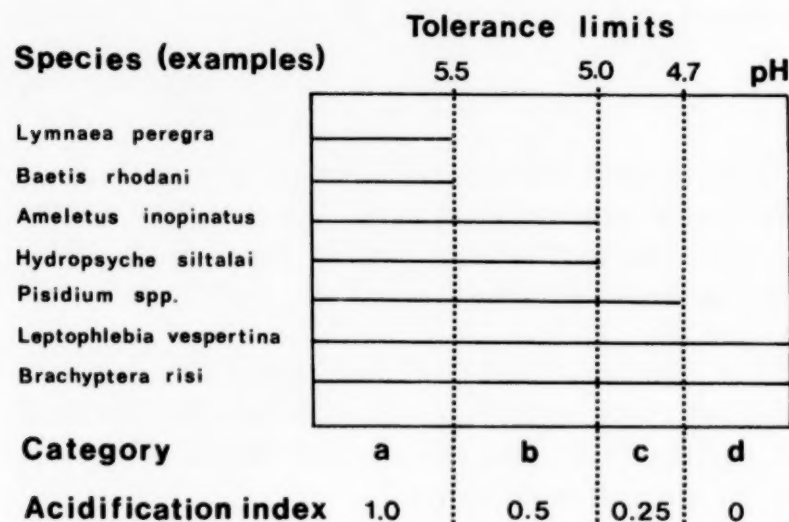


Fig. 2. Relationships between tolerance of acidity and acidification index. According to species composition, each locality is given a value ranging from 1 [unacidified, species in category (a) present] to 0 [highly acidified, only species in category (d) present]. A more extensive list of invertebrates is given in Table 1.

TABLE 1

Acid-sensitive invertebrates used in the monitoring program in Norway. Acidification index tolerance limits are given in Fig. 2

Invertebrate taxa	Index
Turbellaria	
<i>Crenobia alpina</i> (Dana)	0.5
<i>Otomesostoma auditivum</i> (Pless.)	0.5
Bivalvia	
<i>Anodonta</i> sp.	1
<i>Margaritana margaritifera</i> L.	1
<i>Sphaerium</i> spp.	0.5
<i>Pisidium</i> spp.	0.25
Gastropoda	
<i>Lymnaea peregra</i> (Muller)	1
<i>Planorbis</i> spp.	1
Hirudinea	
<i>Helobdella stagnalis</i> (L.)	0.5
<i>Theromyzon tessulatum</i> (O.F. Muller)	1
<i>Glossiphonia complanata</i> (L.)	1
<i>Haemopsis sanguisuga</i> (L.)	1
Crustacea	
<i>Lepidurus arcticus</i> Kroyer	1
<i>Gammarus lacustris</i> Sars	1
<i>Asellus aquaticus</i> (L.)	0.5
<i>Daphnia magna</i> Straus	0.5
<i>Daphnia longispina</i> O.F. Muller	0.5
Ephemeroptera	
<i>Ameletus inopinatus</i> Eaton	0.5
<i>Siphonurus aestivalis</i> (Eaton)	0.5
<i>Siphonurus lacustris</i> Eaton	0.5
<i>Siphonurus linnaeanus</i> (Eaton)	0.5
<i>Baetis rhodani</i> (Pictet)	1
<i>Baetis fuscatus</i> (L.)	1
<i>Baetis lapponicus</i> (Bengts.)	1
<i>Baetis macani</i> Kimmins	1
<i>Baetis muticus</i> (L.)	1
<i>Baetis niger</i> (L.)	1
<i>Baetis scambus</i> Eaton	1
<i>Baetis subalpinus</i> Bengts.	1
<i>Baetis vernus</i> Curtis	1
<i>Heptagenia sulphurea</i> (Muller)	0.5
<i>Heptagenia fuscogrisea</i> (Retz.)	0
<i>Leptophlebia vespertina</i> (L.)	0
<i>Leptophlebia marginata</i> (L.)	0
<i>Ephemerella aurivilli</i> (Bengts.)	1
<i>Ephemerella mucronata</i> (Bengts.)	0
<i>Ephemerella ignita</i> Bengts.	0
<i>Caenis horaria</i> (L.)	1

(continued)

TABLE 1 (continued)

Invertebrate taxa	Index
Plecoptera	
<i>Arcynopteryx compacta</i> (McL.)	0.5
<i>Diura nanseni</i> (Kempny)	0.5
<i>Diura bicaudata</i> (L.)	0.5
<i>Isoperla grammatica</i> (Poda)	0.5
<i>Isoperla obscura</i> (Zett.)	0.5
<i>Dinocras cephalotes</i> (Curt.)	0.5
<i>Siphonoperla burmeisteri</i> (Pict.)	0
<i>Taeniopteryx nebulosa</i> (L.)	0
<i>Brachyptera risi</i> (Mort.)	0
<i>Amphinemura standfussi</i> (Ris)	0
<i>Amphinemura borealis</i> (Mort.)	0
<i>Amphinemura sulcicollis</i> (Stph.)	0
<i>Nemoura cinerea</i> (Retz.)	0
<i>Nemoura avicularis</i> Mort.	0
<i>Nemurella picteti</i> Klap.	0
<i>Protonemu meyeri</i> (Pict.)	0
<i>Capnia atra</i> Mort.	0.5
<i>Capnia pygmaea</i> (Zett.)	0.5
<i>Leuctra digitata</i> Kempny	0
<i>Leuctra fusca</i> (L.)	0
<i>Leuctra hippopus</i> Kempny	0
<i>Leuctra nigra</i> (Oliv.)	0
Trichoptera	
<i>Rhyacophila nubila</i> (Zett.)	0
<i>Glossosoma intermedium</i> Klap.	1
<i>Ithytrichia lamellaris</i> Eaton	0.5
<i>Oxyethira</i> spp.	0
<i>Philopotamus montanus</i> (Donovan)	0.5
<i>Tinodes waeneri</i> (L.)	0.5
<i>Cyrnus flavidus</i> McL.	0
<i>Cyrnus trimaculatus</i> (Curtis)	0
<i>Holocentropus dubius</i> (Rambur)	0
<i>Neureclipsis bimaculata</i> (L.)	0
<i>Plectrocnemia conspersa</i> (Curtis)	0
<i>Polycentropus flavomaculatus</i> (Pict.)	0
<i>Polycentropus irroratus</i> (Curtis)	0
<i>Hydropsyche angustipennis</i> (Curtis)	0.5
<i>Hydropsyche pellucidula</i> (Curtis)	0.5
<i>Hydropsyche siltalai</i> Dohler	0.5
<i>Agrypnia obsoleta</i> Hagen	0
<i>Phryganea grandis</i> L.	0
<i>Lepidostoma hirtum</i> (Fabr.)	0.5
<i>Apatania zonella</i> (Zett.)	0.5
<i>Apatania stigmatella</i> (Zett.)	0.5
<i>Chaetopteryx villosa</i> (Fabr.)	0
<i>Limnophilus centralis</i> Curtis	0
<i>Limnophilus extricatus</i> McL.	0
<i>Limnophilus flavicornis</i> (Fabr.)	0

TABLE 1 (continued)

Invertebrate taxa	Index
<i>Limnephilus lunatus</i> Curtis	0
<i>Limnephilus rhombicus</i> (L.)	0
<i>Limnephilus stigma</i> Curtis	0
<i>Limnephilus vittatus</i> (Fabr.)	0
<i>Halesus radiatus</i> (Curtis)	0
<i>Micropterna lateralis</i> (Steph.)	0
<i>Potamophylax cingulatus</i> (Steph.)	0
<i>Potamophylax latipennis</i> (Curtis)	0
<i>Stenophylax permistus</i> McL.	0
<i>Notidobia ciliaris</i> (L.)	0
<i>Sericostoma personatum</i> (K & Sp.)	0.5
<i>Molanna angustata</i> Curtis	0
<i>Molannodes tinctus</i> (Zett.)	0
<i>Adicella reducta</i> McL.	0
<i>Athripsodes aterrimus</i> (Steph.)	0
<i>Athripsodes cinereus</i> (Curtis)	0
<i>Mystacides azurea</i> (L.)	0

Each locality is given a numeric value according to the species composition, ranging from 1 [unacidified, species in category (a) present] to 0 [highly acidified, only species in category (d) present]. The mean acidification number gives information on the degree of acidification of the watershed. A list of the most common invertebrates used in our study is given in Table 1.

RESULTS

The mean acidification index for the different watersheds during spring and autumn is presented in Fig. 3. The acidification level, based on invertebrate composition, differs over time. Generally, the watersheds in the Farsund area are most acidic, with an acidification index ranging between 0.04 and 0.20.

There was a tendency at the other localities towards a high degree of acidification during the period 1982–1984. This was less pronounced at later times, the only exception is for the River Vikedal in spring 1987. At present, the lower parts of the River Nausta and the River Gaular seem to have a stabilized pH level, indicating no danger to the salmon populations.

DISCUSSION

Since benthic animals show variations in their tolerance to different degrees of acidity, fauna surveys are a very useful tool in acidification monitoring. Widespread species, especially among the mayflies (Raddum and Fjellheim, 1987), are more sensitive to acidification than are the salmonids. The absence of these and other sensitive invertebrates thus serves as an early warning signal of acidification (Raddum and Fjellheim, 1984).

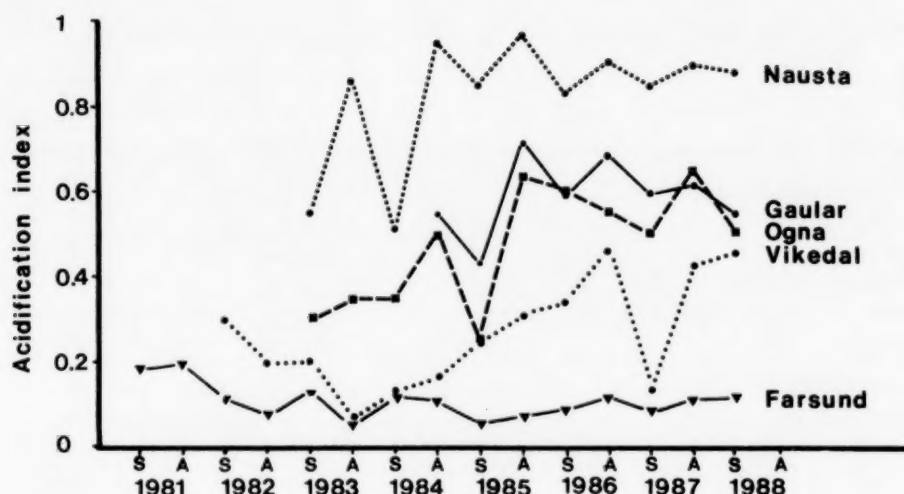


Fig. 3. Mean acidification index of the different watersheds during spring (S) and autumn (A) in the period 1981–1987.

The results of the benthic invertebrate monitoring program indicate a recent improvement in water quality in most of the rivers except those in the Farsund area. Most watersheds are, however, still vulnerable to acid deposition, as indicated by the low index of the River Vikedal in spring 1987. This river has dense populations of acid-sensitive invertebrates in some groundwater tributaries in the middle reach. In the late 1970s, some of these species, especially the mayfly *Baetis rhodani*, also formed strong populations in the lower part of the main river (State Pollution Control Authority, 1984). In spite of the liming of the river, the downstream part has not yet been recolonized by these invertebrates. This is probably due to acid episodes in late summer and autumn which are not effectively limed.

The variations in the acidification index were correlated with the mortality of young salmon in both the River Vikedal and the River Nausta. In the River Vikedal, a total of 270 salmon parr were found dead during 1983 and 1984 (Hesthagen, 1986). Even if the density of age group 1+ reached a minimum value in the River Vikedal in 1983, the densities of fry remained relatively constant. This was explained by the fact that the egg stage is less sensitive than the yolk sac fry stage (Raddum et al., 1988). During the later years, fish mortality in the River Vikedal has been less pronounced.

In the River Nausta the density of the 0+ age group in 1982 was very low, while in 1983 no salmon fry were caught. After 1983, recruitment increased, reaching a maximum value of 27 fish per 100 m² in 1985 (Raddum et al., 1988).

In the other rivers of the invertebrate monitoring program, long-term fish density data are scarce.

Most of the present knowledge on the distribution of freshwater invertebrates according to acidification has accumulated during recent years (Sutcliffe and Carrick, 1973; Englom and Lingdell, 1983; Matthias, 1983; Otto and Svensson, 1983; Raddum and Fjellheim, 1984; Økland and Økland, 1986). Some of these studies have been carried out in water qualities different from the

soft-water conditions in southern Norway. Results indicate that tolerance limits with respect to pH from various geographical regions are not directly comparable, as other water chemistry parameters are of great significance to the physiological response of the animal (Otto and Svensson, 1983; Havas, 1985; Herrmann, 1987; Raddum and Fjellheim, 1987). The tolerance limits of different invertebrate taxa should therefore be tested in different water qualities, in order to improve the precision of the model.

There also exists a need for more ecological and taxonomic knowledge of many invertebrate groups. As an example, improvement in the knowledge of the chironomids could prove to be a valuable tool in invertebrate monitoring, due to their high diversity and density in most localities.

ACKNOWLEDGMENT

This study was financed by the Norwegian Ministry of Environment.

REFERENCES

- Dahl, K., 1927. The effects of acid water on trout fry. *Salmon trout Mag.*, 46: 35-43.
- Engblom, E. and P.E. Lingdell, 1983. Usefulness of the bottom fauna as a pH indicator. Rep. Natl. Swedish Environ. Protect. Board, SNV PM, 1741, Stockholm, 181 pp. (in Swedish with English summary).
- Frost, S., A. Huni and W.E. Kershaw, 1971. Evaluation of a kicking technique for sampling stream bottom fauna. *Can. J. Zool.*, 49: 167-173.
- Haines, T., 1981. Acid precipitation and its consequences for aquatic ecosystems: A review. *Trans. Am. Fish. Soc.*, 110: 669-707.
- Havas, M., 1985. Aluminum bioaccumulation and toxicity to *Daphnia magna* in soft water at low pH. *Can. J. Fish. Aquat. Sci.*, 42: 1741-1748.
- Henriksen, A., 1985. Acid rain and the European situation. In: R.H. Stroud (Ed.), *World Angling Resources and Challenges*. International Game Fish Association, Fort Lauderdale, Florida, pp. 1-11.
- Henriksen, A., E.J.S. Røgeberg, A. Fjellheim, G.G. Raddum, B.O. Rosseland and O.K. Skogheim, 1987. Water chemistry — fish decline: Episodic changes in water quality — Effects on fish and invertebrates. In: B.J. Mason (Ed.), *Surface Water Acidification Programme, Mid-term Review*. The Royal Society, London, pp. 163-176.
- Herrmann, J., 1987. Sodium levels of lotic mayfly nymphs being exposed to aluminum at low pH. A preliminary report. *Ann. Soc. R. Belg.*, 117: 181-188.
- Hesthagen, T., 1986. Fish kills of Atlantic salmon (*Salmo salar*) and brown trout (*Salmo trutta*) in an acidified river of SW Norway. *Water, Air Soil Pollut.*, 39: 619-628.
- Hesthagen, T. and B.M. Mejdell Larsen, 1987. Acidification and Atlantic salmon in Norway. International Council for the Exploration of the Sea. CM 1987/M:28, Copenhagen, pp. 1-19.
- Hesthagen, T., I. Sevaldrud and O.K. Skogheim, 1982. Ognå and Helgaa watersheds. Fish status and water quality. Rep. No. 4. Directorate of Game and Freshwater Fish, Ås (in Norwegian).
- Huitfeldt-Kaas, H., 1922. On the cause of mass kill of salmon and brown trout in Frafjordelven, Hellelven and Dirdalselven, Ryfylke autumn 1920. *Nor. Jæger Fiskerfor. Tidsskr.*, 1: 37-44 (in Norwegian).
- Jensen, K.W. and E. Snekvik, 1972. Low pH levels wipe out salmon and trout populations in southernmost Norway. *Ambio*, 1: 223-225.
- Jonsson, N. and I. Blakar, 1987. Chemical monitoring of Norwegian rivers 1986. Report DN, Fish Res. Division, Trondheim, 1/1987 (in Norwegian).

- Lien, L., 1986. Gaularvassdraget. State Pollution Control Authority. Rep. No. 248, Oslo, 143 pp. (in Norwegian).
- Matthias, U., 1983. Der Einfluss der Versauerung auf die Zusammensetzung von Bergbach-biozosen. Arch. Hydrobiol., Suppl., 65: 407-483.
- Muniz, I.P. and H. Leivestad, 1980. Acidification — effects on freshwater fish. In: D. Drablos and A. Tollan (Eds), Ecological Impact of Acid Precipitation. SNSF Project, Oslo, Ås, pp. 84-92.
- Muniz, I.P., H.M. Seip and I.H. Sevaldrud, 1984. Relationship between fish populations and pH for lakes in southernmost Norway. Water, Air Soil Pollut., 23: 97-113.
- Økland, I. and K.A. Økland, 1986. The effects of acid deposition on benthic animals in lakes and streams. Experientia, 42: 471-486.
- Otto, C. and B.S. Svensson, 1983. Properties of acid brown water streams in South Sweden, Arch. Hydrobiol., 99: 15-36.
- Overrein, L.N., H.M. Seip and A. Tollan, 1980. Acid precipitation, effects on forest and fish. SNSF Project, FR 19/80, Oslo—Ås, 175 pp.
- Raddum, G.G. and A. Fjellheim, 1984. Acidification and early warning organisms in freshwater in western Norway. Verh. Int. Verein. Limnol., 22: 1973-1980.
- Raddum, G.G. and A. Fjellheim, 1985. Monitoring of invertebrates. In: G. Taugbøl (Ed.), State Pollution Control Authority. National Program for Environmental Monitoring. Rep. 201/85, Oslo, 190 pp. (in Norwegian).
- Raddum, G.G. and A. Fjellheim, 1987. Effects of pH and aluminum on mortality, drift and moulting of the mayfly *Baetis rhodani*. Ann. Soc. R. Zool. Belg., 177 (Suppl. 1): 77-87.
- Raddum, G.G., A. Fjellheim and T. Hesthagen, 1988. Monitoring of acidification through the use of aquatic organisms. Verh. Int. Verein. Limnol., 23: 2291-2297.
- Skogheim, O.K., B.O. Rosseland and I. Sevaldrud, 1984. Deaths of spawners of atlantic salmon in river Oga, SW Norway, caused by acidified aluminum-rich water. Rep. Inst. Freshwater Res., Drottningholm, 61: 195-202.
- State Pollution Control Authority, 1984. River Vikedal. Studies of precipitation, water chemistry and biology 1981-1983. Rep. 123/84, Oslo, 160 pp.
- State Pollution Control Authority, 1988. National Program for Environmental Monitoring. Rep. 333/88, Oslo, 242 pp.
- Sutcliffe, D.W. and T.R. Carrick, 1973. Studies on mountain streams in the English Lake District, I: pH, calcium and the distribution of invertebrates in the River Duddon. Freshwater Biol., 3: 437-462.

CONCENTRATIONS OF ATMOSPHERIC SO₂, NO₂ AND DUST IN THE LUBLIN COAL BASIN AREA

ZDZISŁAW KOZAK, ANDRZEJ FIGURSKI, JERZY NIEĆKO, DANUTA KOZAK and
RYSZARD GIERŻATOWICZ

*University of Maria Curie-Skłodowska, Faculty of Chemistry, Department of Chemical
Technology, 3 Maria Curie-Skłodowska Square, 20-031 Lublin (Poland)*

ABSTRACT

This paper presents concentrations of SO₂, NO₂ and total suspended particulates (TSP) in the atmosphere as well as the quantity of dustfall. Air samples were collected periodically over a 1-year period at eight monitoring stations situated in an area of 8 × 8 km², located in the Central Coal Region area of the Lublin Coal Basin.

On the basis of original emission data and Pasquill's formula, computer simulations were performed to obtain the distribution of the annual average concentrations of the studied air pollutants in the Lublin Coal Basin area and its surroundings. In the case of SO₂, good agreement was found between the simulated and analytical results. In the case of NO₂, however, the simulated values computed from emission data were notably lower than those determined by chemical analysis. Probable reasons for such divergence are presented.

Air pollutant concentrations determined both analytically and simulated from emission data were similar to those obtained in work performed 10 years earlier. None exceeded the maximum acceptable concentration (MAC) for protected areas.

INTRODUCTION

In the late 1970s, a project for developing the Lublin Coal Basin (LCB) was accepted. The location of the LCB is shown in Fig. 1. The project included the construction of seven coal mines with a total annual output of 24.6 Mt of coal to be achieved by 1995. Moreover, the project included the construction of an adequate transportation network, infrastructure and coal-fired generating power stations burning 7.8 Mt of coal per year [1]. It is believed that completion of the program could bring about significant and detrimental environmental changes [1, 2]. This study was undertaken in order to investigate these changes, and motivation was strengthened by the fact that, 10 years earlier, similar studies had been conducted in the same area [3]. The main purpose of these studies was to collect current data for principal air pollutant concentrations, i.e. SO₂, NO₂ and total suspended particulates (TSP), in the LCB region. These SO₂, NO₂ and TSP concentrations were established in two ways: (i) direct measurements in the field, and (ii) computer simulations using emission data as input. Moreover, comparisons were possible between the results of annual average pollutant concentrations determined analytically and those obtained

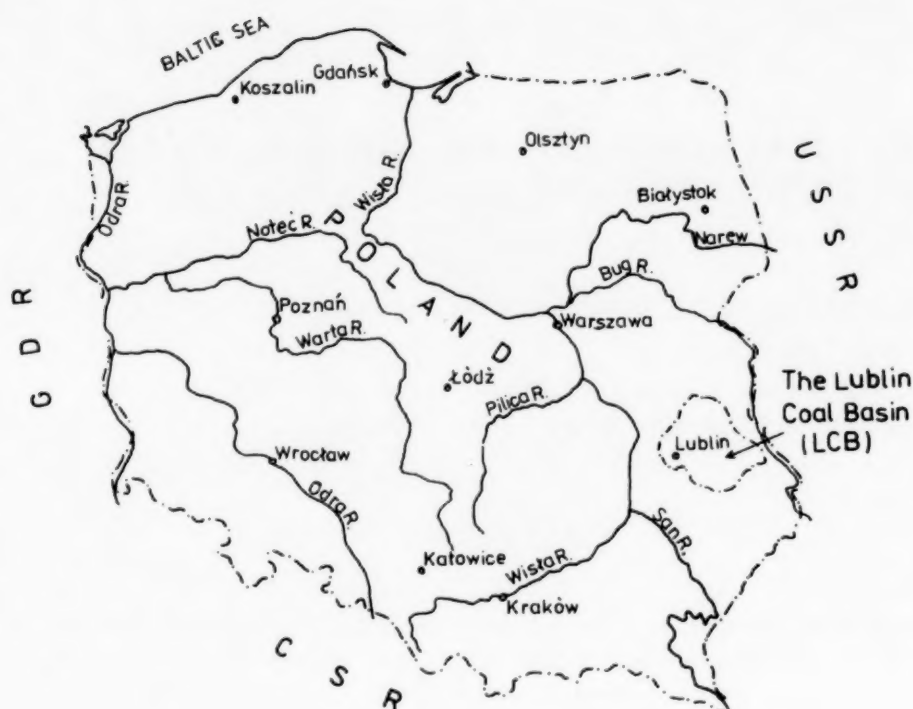


Fig. 1. Location of the Lublin Coal Basin (LCB), Poland.

from the computer model 'Chimney' (in Polish 'Komin') based on emission data [4]. The Chimney program was approved by the Institute of Environmental Protection in Warsaw.

EXPERIMENTAL

The SO_2 , NO_2 and TSP concentrations and the quantity of dustfall were determined at eight stations situated in an area of $8 \times 8 \text{ km}^2$, located in the Central Coal Region (CCR) of the LCB area (Fig. 2).

A set of consecutive dates for collecting air and dustfall samples was chosen at random based upon golden numbers. Detailed information on the monitoring/measurement and ballot procedures is given elsewhere [5].

Sulfur dioxide was determined using the West-Geak procedure [6] and nitrogen dioxide following the method of Saltzman [7]. The TSP concentration was determined by weighing polypropylene filters through which air had been passed for 30 min [8]. Reflection spectroscopy was employed for the 24-h TSP measurements in which paper filters were used. The quantity of dustfall was determined by weighing the solid deposit collected in a jar placed 1.5 m above ground level. The chemical composition of dustfall samples was determined by optical spectroscopy using a Zeiss spectrograph PGS-2. The internal standard addition method was used and each sample was analyzed in triplicate. Detection limits (ppm)/accuracy (%) were: Cd, 1/27; Pb, 4/39; Mn, 20/10; Cr, 4/13; V, 4/22; Cu, 1/18; Zn, 10/18; Ni, 2/18; Hg, qualitative data.

Pollutant concentrations were also computed from pollutant emissions based on data published earlier by Figurski [9] who listed 980 actual main

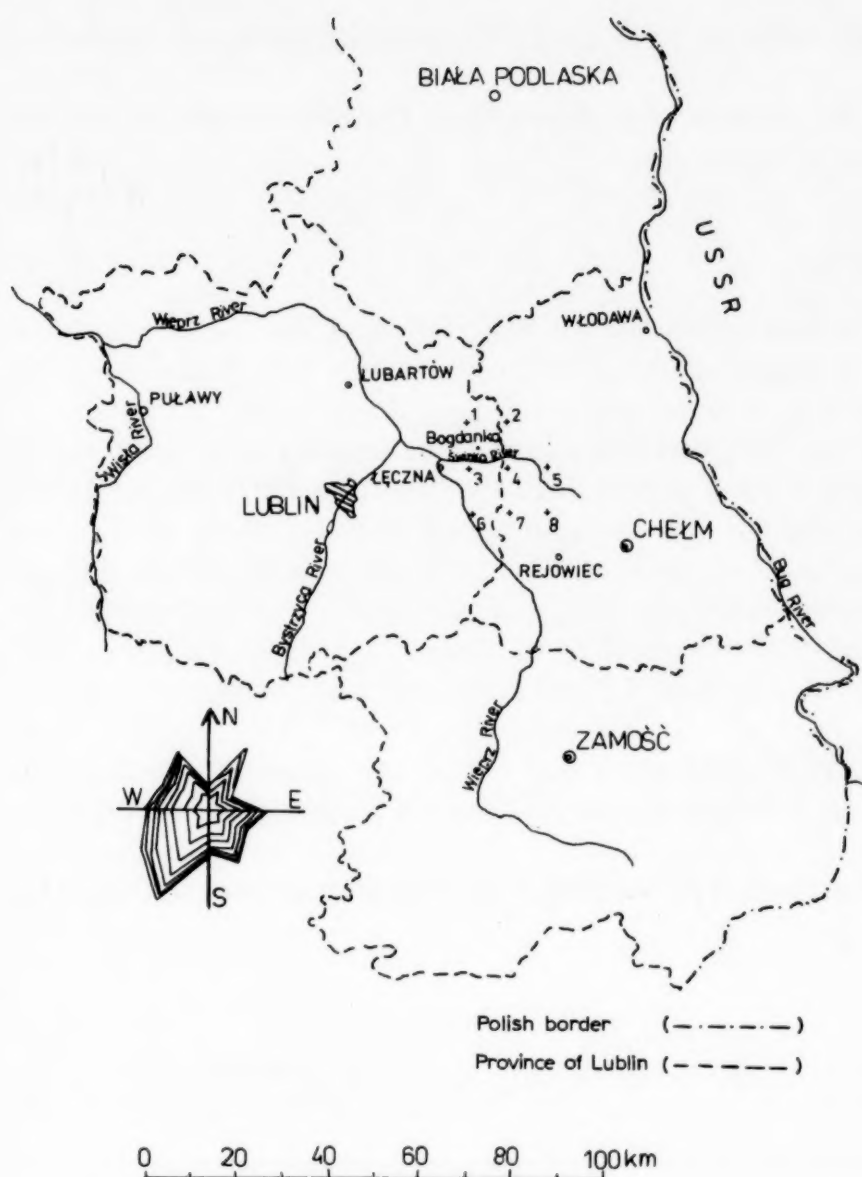


Fig. 2. Measurement points situated in the Central Coal Region of the LCB. (1) Rogóżno; (2) Grabniak; (3) Brzeziny; (4) Głębokie; (5) Syczyn; (6) Jaszczów; (7) Chojeniec; (8) Mogielnica.

emission sources of SO_2 , NO_2 , CO and TSP in the LCB region and its surroundings. The computational method is described in directives from the Ministry of Administration, Field Economics and Environmental Protection, issued in 1981/1983 [10]. The computer program 'Chimney', based on Pasquill's formula, was developed according to these directives. In order to simplify the simulation, the 980 emission sources were grouped into 85 sets, each of which was then treated as a single emitter. The data set with meteorological conditions, i.e. wind speed, direction, frequency and atmospheric stability class, required by the model was derived from a database annexed to the directives. The database for Lublin utilizes 21 408 measurements provided by synoptic sampling by the Institute of Meteorology and Water Economics, and

covers the period from 1966 to 1975 [11]. The simulation area comprises $\sim 5000 \text{ km}^2$.

For this simulation, for a regional problem, both Pasquill's formula and the Chimney program could be used.

RESULTS AND DISCUSSION

The results of the 24-h measurements for SO_2 , NO_2 and TSP concentrations in air from the Bogdanka region, carried out between July 1987 and June 1988, are presented in Tables 1–3, respectively.

Table 4 presents results obtained from statistical treatment of the data in Tables 1–3 and the results for the period July 1986 to June 1987. NO_2 and NO_x concentrations are expressed in all cases in terms of N_2O_5 . Data in Table 4 indicate that, in 1987–1988, there was an insignificant excess in the annual average acceptable concentration of NO_2 , i.e. $28 \mu\text{g m}^{-3} \pm 20\%$ versus the accepted value of $22 \mu\text{g m}^{-3}$. The numerical values of $P_{D_{24}}$, S_{98} and S_{\max} for NO_2 were all below the accepted values of 0.2%, 0.15 mg m^{-3} and 0.3 mg m^{-3} , respectively.

For the period 1986–1987, TSP excesses (Table 4) occurred for annual average concentration (D_a) and frequency of excess in acceptable 24-h concentration ($P_{D_{24}}$).

In all cases, it was observed that the NO_2 concentrations exceeded the SO_2

TABLE 1

Results of 24-h measurements of SO_2 concentrations ($\mu\text{g m}^{-3}$) in the Bogdanka area

Date	Site			
	Brzeziny	Głębokie	Grabniak	Rogóżno
16 July 87	1	5	4	4
20 Aug. 87	0	0	0	0
22 Sept. 87	0	0	0	0
8 Oct. 87	1	2	5	1
10 Nov. 87	260	69	73	3
10 Dec. 87	8	NA	11	17
7 Jan. 88	1	0	0	0.5
9 Feb. 88	5	38	36	11
2 Mar. 88	6	30	13	9
28 Mar. 88	1	NA	NA	2
20 Apr. 88	1	2	1	3
3 May 88	0	0	0	0
23 May 88	0	0	0	0
9 June 88	0	0	0	0
30 June 88	4	3	1	1

NA = not available.

TABLE 2

Results of 24-h measurements of NO_2 concentrations, expressed in terms of N_2O_5 ($\mu\text{g m}^{-3}$), in the Bogdanka area

Date	Site			
	Brzeziny	Głębokie	Grabniak	Rogóżno
16 July 87	28	23	8	14
20 Aug. 87	24	14	13	9
22 Sept. 87	51	14	6	5
8 Oct. 87	22	20	8	NA
10 Nov. 87	127	9	16	8
10 Dec. 87	35	75	93	40
7 Jan. 88	20	25	13	17
9 Feb. 88	8	22	15	8
2 Mar. 88	6	2	1	75
28 Mar. 88	16	39	27	11
20 Apr. 88	19	21	12	11
3 May 88	NA	84	87	5
23 May 88	8	9	87	8
9 June 88	14	35	24	22
30 June 88	24	41	48	53

NA = not available.

TABLE 3

Results of 24-h measurements of total suspended particulate concentrations ($\mu\text{g m}^{-3}$) in the Bogdanka area

Date	Site			
	Brzeziny	Głębokie	Grabniak	Rogóżno
16 July 87	3	6	2	45
20 Aug. 87	1	0	2	5
22 Sept. 87	11	34	7	10
8 Oct. 87	23	40	62	8
10 Nov. 87	NA	NA	NA	NA
10 Dec. 87	16	NA	18	9
7 Jan. 88	25	NA	NA	30
9 Feb. 88	3	62	NA	12
2 Mar. 88	9	99	50	6
28 Mar. 88	9	NA	NA	12
20 Apr. 88	5	12	3	7
3 May 88	4	18	2	2
23 May 88	3	7	2	3
9 June 88	3	5	13	6
30 June 88	4	8	3	4

NA = not available.

TABLE 4

Results of statistical computation of 24-h measurements of air pollutants in the Bogdanka area (reference station 1)

Pollutant	D_a (mg m^{-3})	S_m	S_1	$P_{D_{24}}$ (%)	S_{98} (mg m^{-3})	S_{\max} (mg m^{-3})	> MAC (%)	< 0.5 MAC (%)
Between July 1986 and June 1987								
SO ₂	0.012	0.001	0.93	0	0.081	0.54	0	100
NO ₂	0.016	0.011	0.39	3.4	0.068	0.15	2	93
TSP	0.035	0.009	0.71	7.3	0.260	1.11	6	92
Between July 1987 and June 1988								
SO ₂	0.024	0.001	1.04	0	0.130	1.10	0	98
NO ₂	0.028	0.019	0.39	0	0.120	0.26	0	91
TSP	0.018	0.008	0.56	0	0.110	0.34	0	98

D_a = annual average concentration; S_m = median; S_1 = standard deviation; $P_{D_{24}}$ = frequency of excesses in acceptable 24-h concentrations; S_{\max} = maximum concentration; S_{98} = concentration that is not exceeded for 98% of the year; > MAC = percentage of results that exceed MAC; < 0.5 MAC = percentage of results that are lower than one-half of MAC.

TABLE 5

Distribution of instantaneous concentrations of air pollutants in the LCB area

Reference point ^a (x)	Pollutant	Arithmetic mean (mg m ⁻³)	S _m	S ₁	P _{D30} (%)	> MAC (%)	In excess of MAC by (%)	< 0.5 MAC (%)
Between July 1986 and June 1987								
1	SO ₂	0.17	0.021	0.93	4.6	3	10	93
	NO ₂	0.20	0.16	0.29	4.5	3	113	75
	TSP	0.32	0.23	0.36	18.0	15	178	53
Between July 1987 and June 1988								
1	SO ₂	0.09	0.027	0.67	0	0	0	100
	NO ₂	0.18	0.15	0.25	3	1.7	25	81
	TSP	0.45	0.25	0.47	30	29	108	54
2	SO ₂	0.13	0.017	0.87	0	0	0	100
	NO ₂	0.18	0.16	0.24	3	1.7	45	83
	TSP	0.39	0.26	0.40	30	29	90	42
3	SO ₂	0.13	0.021	0.83	0	0	0	98
	NO ₂	0.19	0.17	0.23	0	0	0	80
	TSP	0.45	0.27	0.44	33	32	132	45

^a x = reference points were obtained from measurement points located at the following sites: (1) Brzeziny, Głębokie, Grabniak and Rogóżno; (2) Brzeziny, Głębokie, Jaszczów and Chojeniec; (3) Chojeniec, Głębokie, Mogielnica and Syczyn.

concentrations. The same observation was noted earlier for Czechoslovakia [12] and the southwestern U.S.A. [13].

In the vicinity of the research area, regional parks, health resorts and recreational areas exist or are planned. The air pollutant concentrations recorded and presented in Tables 1–4 should therefore be regarded as relatively high when compared with the MACs. It should be noted that MACs for specially protected areas are 10 times lower than those for other areas.

Apart from 24-h measurements, 30-min measurements were taken at dates and times chosen at random, according to golden numbers. The results of the 30-min measurements were grouped to give three reference points. The data were then processed statistically and the final results are presented in Table 5. These results show that, although some exceed $P_{D_{30}}$ (especially TSP), the average concentrations of SO_2 , NO_2 and TSP are lower than the MACs.

Table 6 presents data for average 30-min measurements recorded at the eight locations shown in Fig. 2. The results show that differences in air pollutant concentrations between these sites were not great.

Table 7 summarizes annual average concentrations of SO_2 , NO_x , TSP and CO calculated from emission data for stationary sources by means of the Chimney model. It also shows the maximum instantaneous concentrations (30-min) that can occur under the most unfavourable meteorological conditions and the highest emission from all emitters.

When the data in Table 7 are compared with those in Table 4, it can be seen that the simulated concentrations are always lower than those established analytically. In the case of SO_2 they are $12.0\text{--}24.0\ \mu\text{g m}^{-3}$ (anal.) and $8.8\text{--}13.6\ \mu\text{g m}^{-3}$ (sim.). For NO_x the results are $16.0\text{--}28.0\ \mu\text{g m}^{-3}$ (anal.) and $2.4\text{--}4.0\ \mu\text{g m}^{-3}$ (sim.), and for TSP, $18.0\text{--}35.0\ \mu\text{g m}^{-3}$ (anal.) and $3.9\text{--}6.2\ \mu\text{g m}^{-3}$ (sim.). The simulated and measured concentrations are roughly in agreement only for the annual SO_2 concentration.

Differences between pollutant concentrations determined analytically and those determined via computer simulation arise, first of all, from problems caused by disregarding non-stationary and dispersed emission sources such as

TABLE 6

Arithmetic means of SO_2 , NO_2 and TSP concentrations calculated from fifteen 30-min measurements carried out at each measurement point over a period of 1 year

Pollutant ($\mu\text{g m}^{-3}$)	Site ^a							
	Br.	Gł.	Gr.	Ro.	Ch.	Ja.	Mo.	Sy.
SO_2	37	44	62	62	89	57	74	49
NO_2	174	164	209	176	208	192	179	
TSP	326	475	309	306	321	242	441	241

^a Br., Brzeziny; Gł., Głębokie; Gr., Grabniak; Ro., Rogóżno; Ch., Chojeniec; Ja., Jaszczów; Mo., Mogielnica; Sy., Syczyn.

TABLE 7

Results of computer simulations of annual average and maximum concentrations at measurement stations, based on the quantity of pollutant emitted

Location	Annual average conc. ($\mu\text{g m}^{-3}$)				Maximum conc. (mg m^{-3})	
	SO ₂	NO _x	TSP	CO	SO ₂	NO _x
Brzeziny	13.7	3.5	5.3	5.5	0.59	0.46
Głębokie	11.5	3.1	5.5	3.0	0.89	0.44
Grabniak	9.6	2.7	3.9	3.2	0.60	0.28
Rogóżno	12.2	3.0	4.7	7.0	0.54	0.37
Mogielnica	12.3	2.5	6.2	2.7	1.45	0.68
Syczyn	8.8	2.4	4.2	2.6	1.20	0.55
Jaszców	12.3	4.0	4.9	5.3	0.60	0.32
Chojeniec	13.6	3.2	4.6	3.6	0.92	0.27

transportation vehicles, emission from soil, etc. Therefore, the observed divergences are greater for NO₂ than for SO₂.

Divergences in the TSP levels seem to be caused by the occurrence of considerable aeolian erosion, mainly during periods of drought and during heavy agricultural tilling of the soil.

Computer simulations have an advantage over chemical analyses by allowing the examination of large areas at relatively low costs. Therefore, even simple models such as that used here are valuable. If, for example, computer simulations indicate excesses in acceptable concentrations, these will probably be confirmed by chemical analyses.

The data in Table 8 show the quantities of monthly and annual dustfall. The lowest annual dustfall recorded was 36 Mg km⁻² year⁻¹ at two sites, Syczyn and Rogóżno. The highest was 73 Mg km⁻² year⁻¹ at Głębokie, which is in the range 48–141 Mg km⁻² year⁻¹ reported earlier by Krupka et al. [3]. (see footnote to Table 10).

The approximate chemical composition of dustfall samples is presented in Table 9. The increased cadmium concentrations found at some localities situated to the northeast of Lublin and Łeczna are probably due to the prevalence of westerly winds, which carry pollutants emitted by metallurgical and cadmium pigment works located in the eastern part of Lublin.

For comparative purposes, the results of 20-min measurements of SO₂ and NO₂ concentrations obtained 10 years earlier by Krupka et al. [3] are given in Table 10. These data are comparable to the more recent results only if one takes into account the fact that they differ in measurement duration (20 and 30 min, respectively). The 20-min measurement periods applied in the past are consistent with the former Polish measurement standards for air pollutants

TABLE 8

Dustfall in the LCB area

Measure- ment period	Site ^a and amount of dustfall (Mg km ⁻² month ⁻¹)							
	Br.	Gł.	Gr.	Ro.	Ch.	Ja.	Mo.	Sy.
22 May-25 June 87	5.6	23.9	3.9	4.4	NA	NA	NA	NA
26 June-16 July 87	5.9	5.5	3.9	4.5	NA	NA	NA	NA
17 July-20 Aug. 87	7.4	7.1	3.8	4.5	9.4	10.7	NA	NA
21 Aug.-22 Sept. 87	3.0	4.7	12.4	5.5	4.6	4.6	3.9	4.9
23 Sept.-10 Nov. 87	4.4	3.9	3.5	3.2	6.2	4.3	7.0	3.6
11 Nov.-10 Dec. 87	3.8	4.2	1.6	1.1	0.7	4.5	NA	1.2
11 Dec.-7 Jan. 88	3.8	4.3	2.0	1.5	1.0	4.5	2.0	4.5
8 Jan.-9 Feb. 88	1.1	1.1	1.6	0.7	0.7	2.0	1.2	0.8
10 Feb.-2 Mar. 88	1.6	1.9	1.7	0.9	0.8	2.3	1.5	1.0
3 Mar.-28 Mar. 88	2.3	5.4	2.3	2.4	2.6	3.1	3.0	2.6
29 Mar.-20 Apr. 88	2.7	5.8	3.0	3.2	3.1	3.5	3.2	2.8
24 May- July 88	NA	NA	NA	NA	3.2	7.3	5.8	4.5
Annual av- erage	47	73	39	36	40	58	45	36

^a Br., Brzeziny; Gł., Głębokie; Gr., Grabniak; Ro., Rogóżno; Ch., Chojeniec; Ja., Jaszców; Mo., Mogielnica; Sy., Syczyn. NA = not available.

TABLE 9

Concentration of some heavy metals (ppm) in dry dustfall^a determined by optical spectroscopy

Location	Cd	Pb	Mn	Cr	V	Cu	Zn	Ni	Hg
Brzeziny	250	440	725	62	23	145	2630	24	D
Głębokie	9	140	225	40	17	62	1120	12	D
Grabniak	60	150	540	34	8	55	2300	9	ND
Rogóżno	3	95	160	59	44	52	1000	19	D
Chojeniec	250	325	470	72	37	135	1520	32	ND
Jaszców	30	71	290	28	10	87	890	14	ND
Mogielnica	250	850	780	62	47	205	1550	29	ND
Syczyn	250	460	795	58	26	180	1150	23	ND

^aDustfall samples were collected in the autumn period, 15 Sept.-25 Nov. 1987.

ND = not detectable.

D = qualitative detection. The Hg concentration was ≥ 30 ppm.The bulk of the dustfall samples comprised the following elements: Si, ~ 10 wt%; Al, from 5 to 10 wt%; Na plus K, ~ 2 wt%; Ca, from 0.5 to 5 wt%; and Fe, ~ 1 wt%.

TABLE 10

Results of measurements^a of SO₂ and NO₂ concentrations in air in the LCB area, carried out between July 1975 and June 1976

Measurement point	Concentration ($\mu\text{g m}^{-3}$)			
	SO ₂		NO ₂	
	Winter	Summer	Winter	Summer
A	300	250	200	200
B	300	260	300	100
C	320	167	300	246
D	227	160	222	209
E	300	250	NA	210
F	260	200	400	NA

^a Measurements were carried out by M. Krupka and co-workers according to Polish Standard PN 68/Z-040-39; 20-min measurements were applied. At that time, the dustfall in this area ranged from 48 to 141 Mg km⁻² year⁻¹ [3].

NA = not available.

(PN68/Z-040-39). The results in Table 10 reveal that no significant changes in pollutant concentrations have occurred.

Isolines of annual average concentrations of SO₂, NO_x, CO and TSP, and maximum concentrations of SO₂ and NO_x simulated by the Chimney model for the LCB area are shown in Figs 3-8, respectively. The Chimney simulations suggest that concentrations in excess of the MAC could occur in Lublin, Lubartów, Chelm and Rejowiec, but these localities were not part of the studies described here.

CONCLUSIONS

(i) The atmospheric NO₂ concentrations are higher than those for SO₂ in the area studied. A probable reason is that there are no significant SO₂ sources in this area, and "imported" SO₂ is rapidly oxidized.

(ii) There are no significant excesses in air pollutant concentrations in the LCB area above the acceptable criteria levels for protected areas. Nevertheless, even a small increase in air pollutant emissions could lead to such excesses.

(iii) Air pollutant concentrations established chemically and those derived from the Chimney model simulations are in best agreement for SO₂.

(iv) The analytically determined NO₂ and TSP concentrations are considerably higher than the simulated values.

(v) The divergences mentioned in (iv) above result from the difficulties in taking into consideration all emission sources and the level of NO₂ and TSP emitted from them.

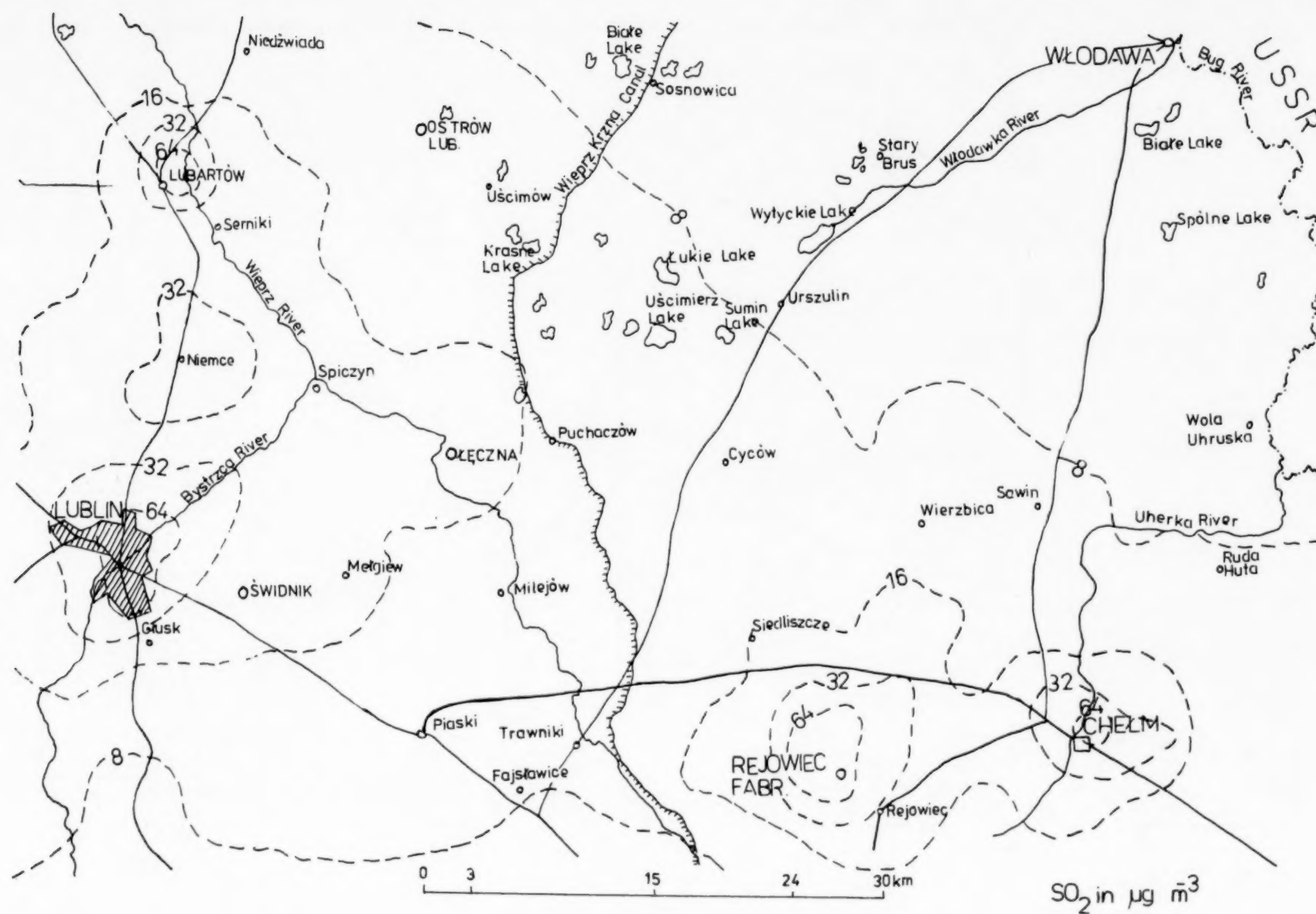


Fig. 3. Isolines of annual average SO_2 concentrations calculated by means of the Chimney computer program.

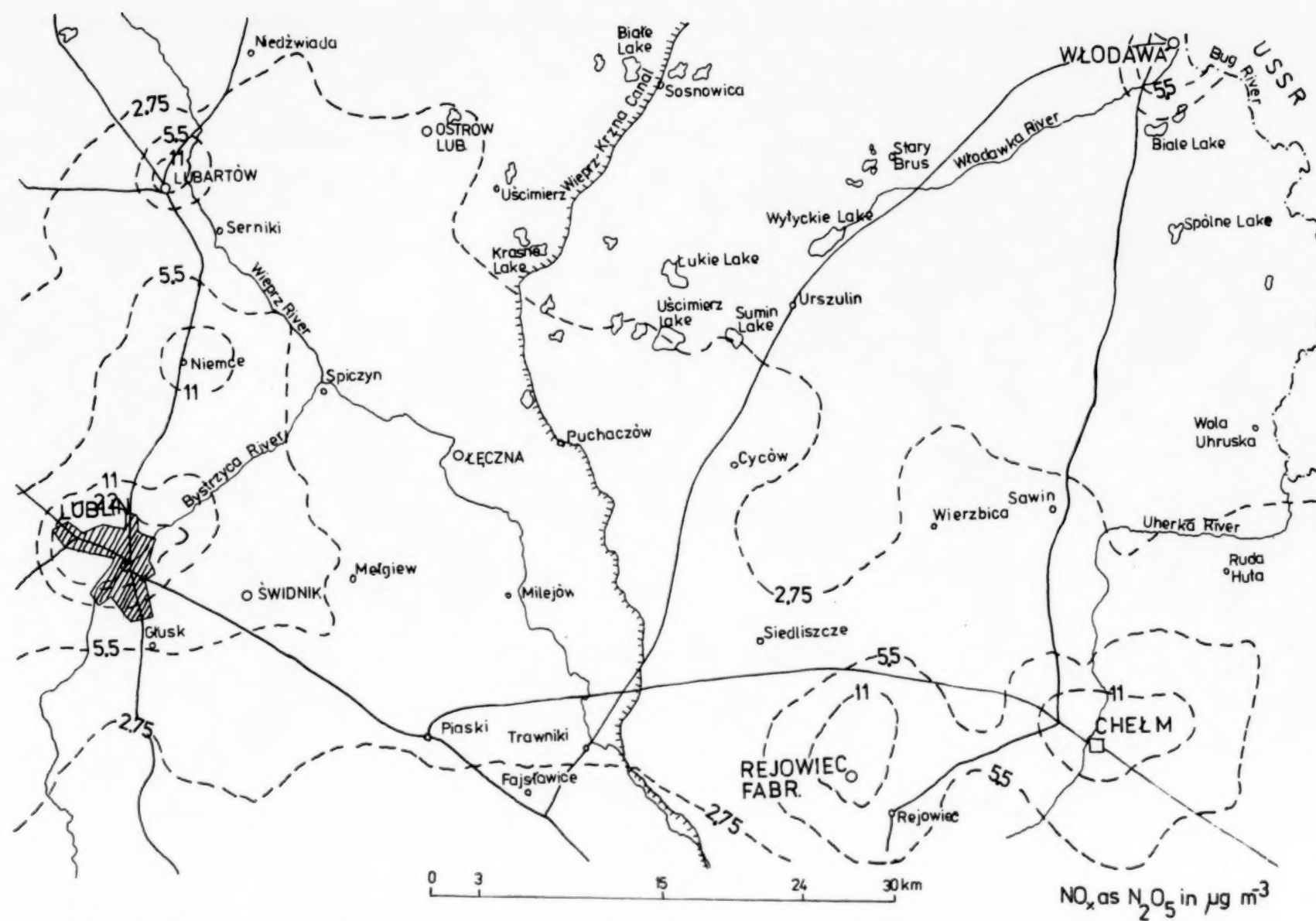


Fig. 4. Isolines of annual average NO_x concentrations calculated by means of the Chimney computer program.

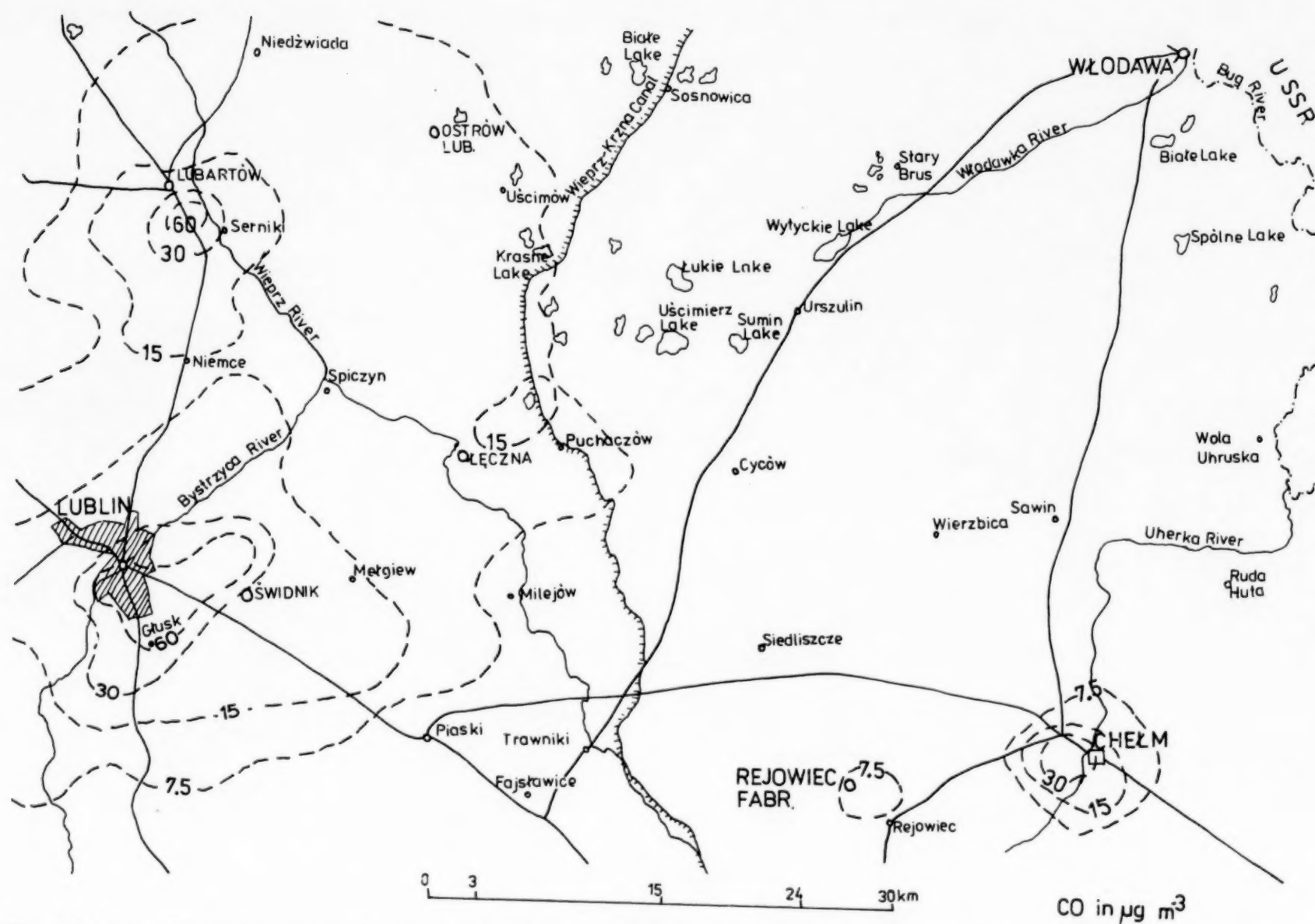


Fig. 5. Isolines of annual average CO concentrations calculated by means of the Chimney computer program.

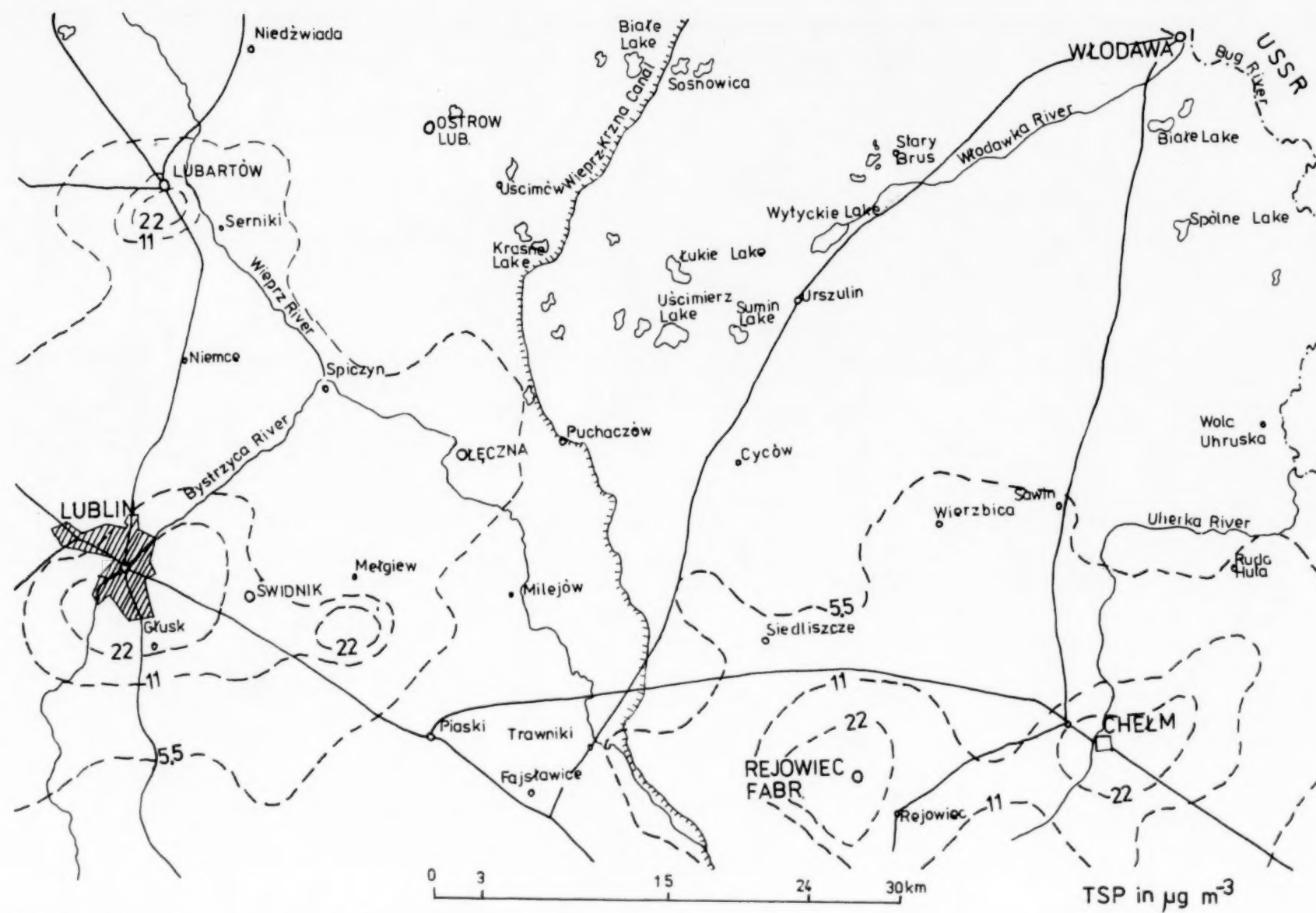


Fig. 6. Isolines of annual average TSP concentrations calculated by means of the Chimney computer program.

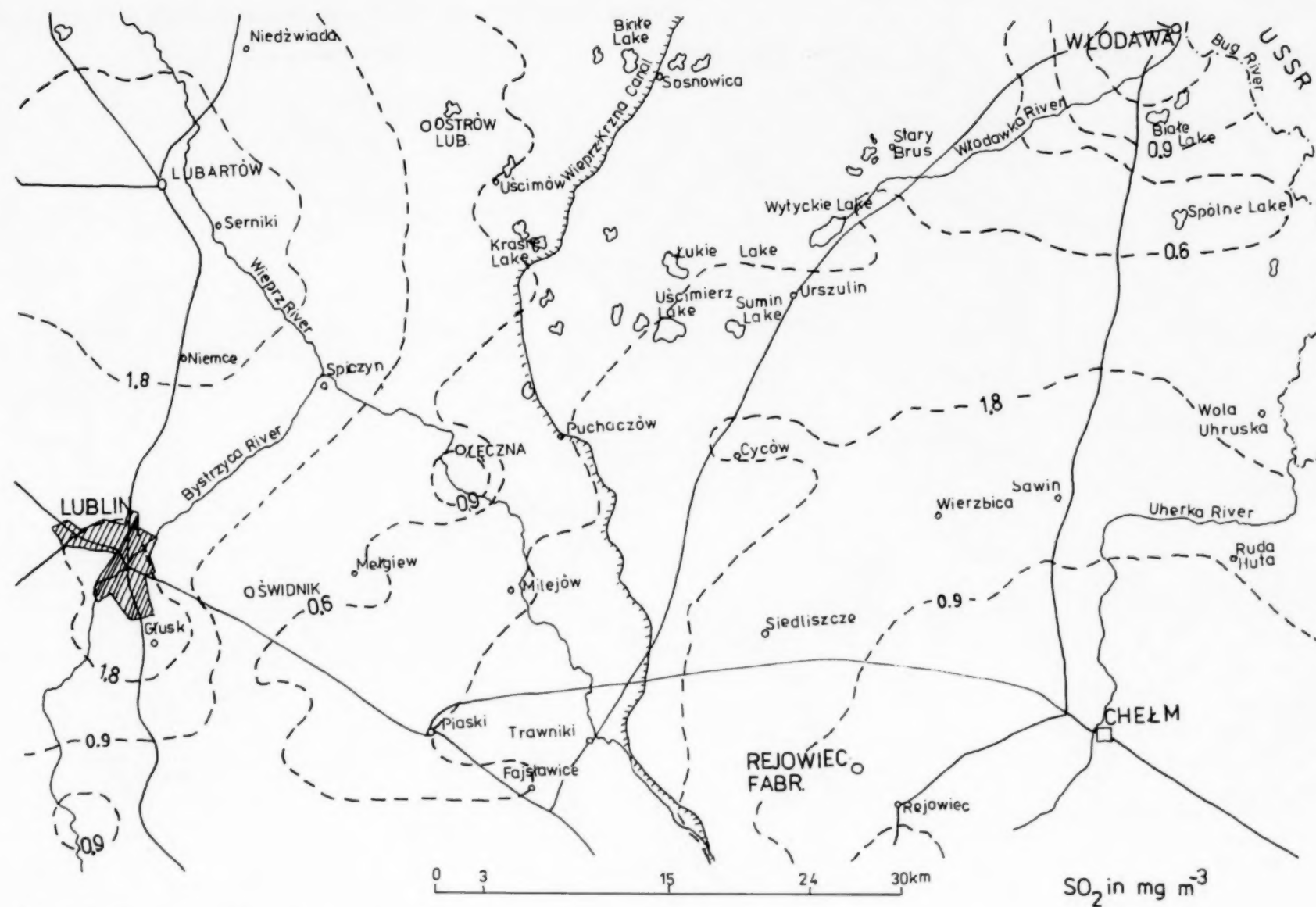


Fig. 7. Isolines of maximum instantaneous SO_2 concentrations (30-min).

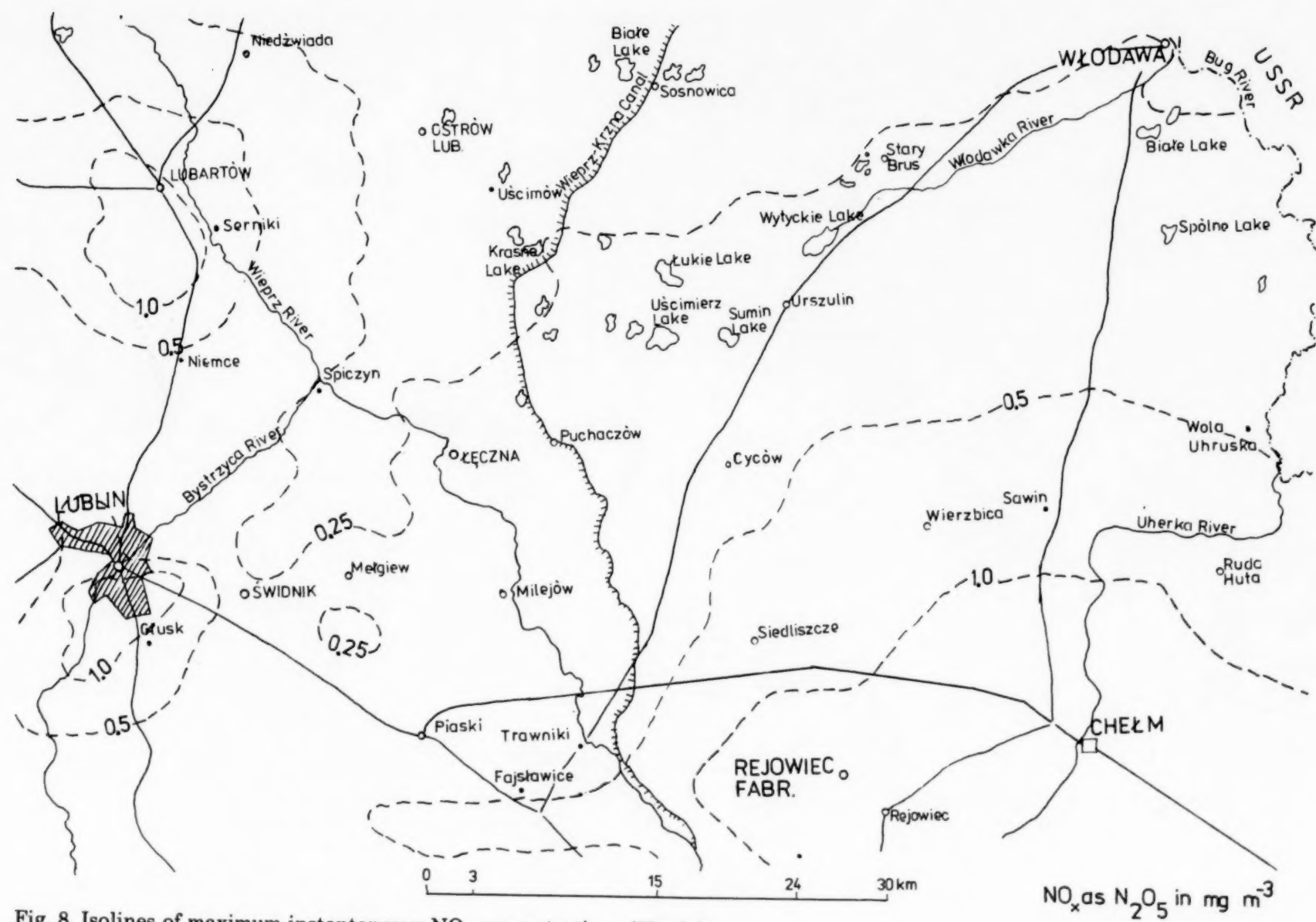


Fig. 8. Isolines of maximum instantaneous NO_x concentrations (30-min).

(vi) The analytically determined NO_2 concentrations are relatively high when compared with the Polish standard for MACs. Nitrogen oxides and dust are probably the main air pollutants in the LCB.

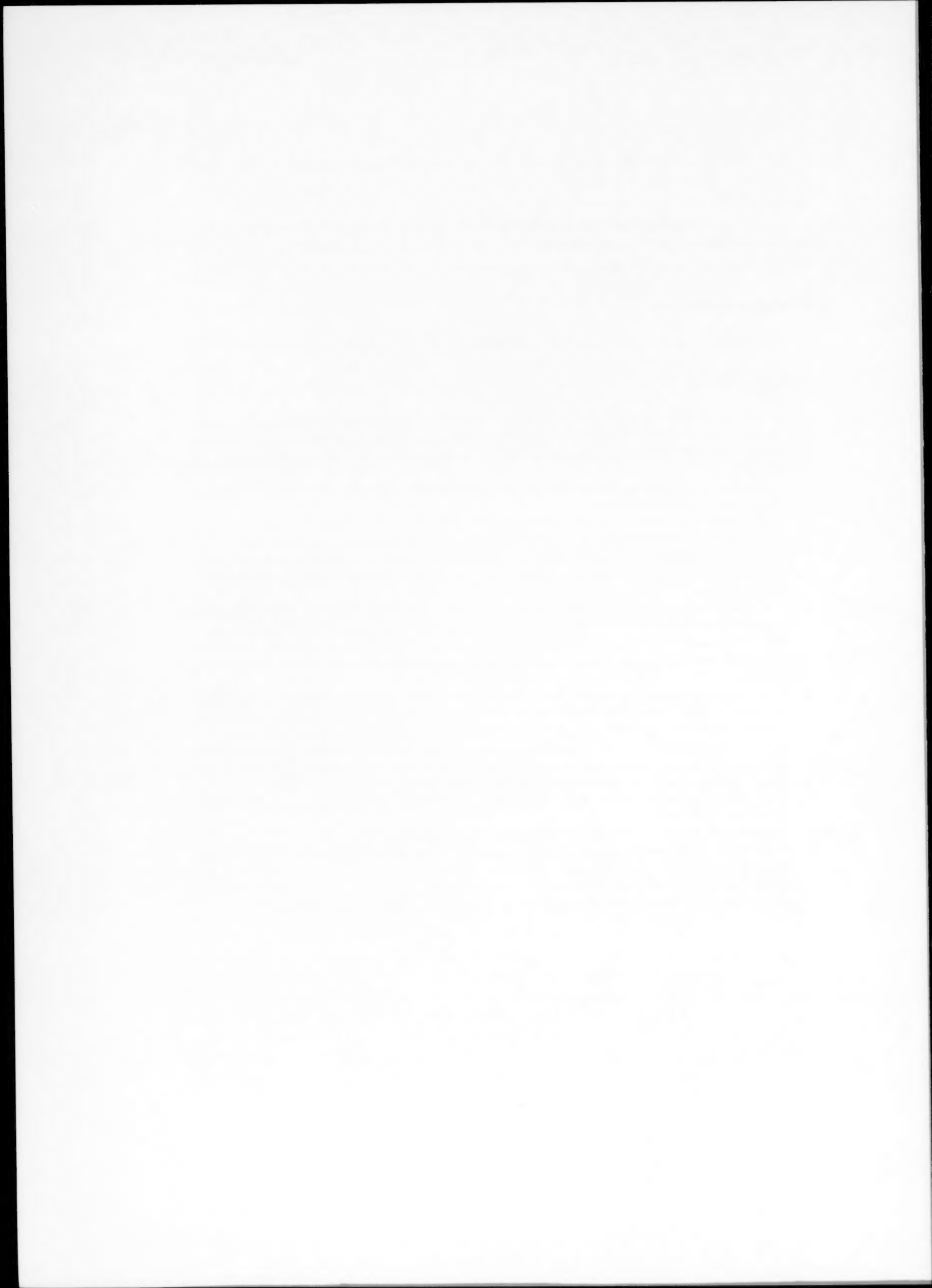
(vii) The Chimney model would be more useful if separate studies could determine the fraction of total NO_2 and dust concentrations resulting only from non-stationary sources such as transportation vehicles and soil.

ACKNOWLEDGEMENT

Financial support under grant CPBP 04.10.05.16 is fully acknowledged.

REFERENCES

- 1 Z. Kozak and D. Kozak, Zanieczyszczenia atmosfery w regionie Lubelskiego Zagłębia Węglowego. Określenie dróg przenoszenia biotycznego i ekologicznego głównych polutantów w regionie LZW, Wydawnictwa Uczelniane Politechniki Lubelskiej, Lublin, Vol. I, 1987, pp. 270-300.
- 2 J. Paździora, Górnicze zagospodarowanie Lubelskiego Zagłębia Węglowego. Seminar Proceedings. Zagłębocze, 1983.
- 3 M. Krupka, E. Kostow and J. Woronko, Medycyna Wiejska, 1978, XII NS, p. 217.
- 4 J. Iwanek, Institute of Environmental Protection, Warsaw, personal communication.
- 5 J. Juda, J. Jędrzejewski and M. Nowicki, Metodyka pomiarów zanieczyszczeń powietrza atmosferycznego. Organizacja sieci pomiarowej i opracowywanie wyników, Ossolineum, Wrocław, 1969.
- 6 P.W. West and G.C. Gaeke, Anal. Chem., 28 (1956) 1816. Zbiór Polskich Norm, Ochrona czystości powietrza, cz. II. Wydawnictwa Normalizacyjne, Warszawa, 1982, PN-76/Z-04104.
- 7 B.E. Saltzman, Anal. Chem., 26 (1954) 1949. J. Paluch and H. Siekieryńska, Metodyka pomiarów zanieczyszczeń powietrza, Metodyka oznaczania tlenków azotu, Ossolineum, Wrocław, 1970.
- 8 D. Kozak and Z. Kozak, Metodyka badań głównych zanieczyszczeń powietrza atmosferycznego na terenie LZW. Określenie dróg przenoszenia abiotycznego i ekologicznego głównych polutantów w regionie LZW, Vol. II, Wydawnictwa Uczelniane Politechniki Lubelskiej.
- 9 A. Figurski, Emisja Źródeł zanieczyszczeń przemysłowych w rejonie LZW, in Określenie dróg przenoszenia abiotycznego i ekologicznego głównych polutantów w regionie LZW, Vol. I, and Metody obliczania stanu zanieczyszczenia atmosfery, Vol. II, in press.
- 10 Wytyczne obliczania stanu zanieczyszczenia powietrza atmosferycznego, MAGTiOS, Warszawa, 1981/1983.
- 11 Meteorological Data Catalogue of MAGTiOS, Warszawa, 1981/1983.
- 12 J. Babusik, M. Cernovsky and D. Zavodsky, Seminar Proc., Interekotechnika 86, Bratislava, June 1986.
- 13 NAPAP Interim Assessment, Atmospheric Processes and Deposition, Ch.N. Henick and J.L. Kulp (Eds), U.S. Government Printing Office, Washington, DC, Vol. III, 1988, pp. 5-18.



CALCULATIONS OF LONG-RANGE TRANSPORTED SULPHUR AND NITROGEN OVER EUROPE

TROND IVERSEN

The Meteorological Synthesizing Centre — West (MSC-W) of EMEP, The Norwegian Meteorological Institute, P.O. Box 43, Blindern, N-0313 Oslo 3 (Norway)

ABSTRACT

The ECE Executive Body for the convention on long-range transboundary air pollution has included the estimation of transboundary nitrogen oxides into the EMEP (European Monitoring and Evaluation Programme). A model aimed at this estimation has been developed. The model is Lagrangian and includes the chemistry for 10 components. Model-estimated budgets for deposition of oxidized sulphur and oxidized and reduced nitrogen in Poland and Norway in 1985 are presented. The calculations show that Poland emitted about twice as much as was received of each of these three components. Norway emitted much less (25%) sulphur than was received and about the same amount of nitrogen compounds. For sulphur and reduced nitrogen, more than half of the deposition in Poland was due to internal emissions, while the corresponding figures for Norway were about 5 and 25%, respectively. For oxidised nitrogen, about 25% of the depositions in Poland originated from Poland and 20% from the Federal Republic of Germany. In Norway, about 10% of the depositions of oxidised nitrogen are due to Norwegian emissions. The budget reflects the fact that sulphur depositions in Europe are dominated by Eastern Europe emissions, while depositions of oxidised nitrogen are dominated by Western European emissions.

INTRODUCTION

The modelling of the transport of oxidised nitrogen is far more complex than the corresponding modelling of oxidised sulphur. The SO_2 -sulphate chemistry can, with reasonable accuracy, be simplified to a linear oxidation of SO_2 directly to particulate sulphate with no other components taken into account. Such modelling has been performed with considerable success (Eliassen, 1978; Eliassen and Saltbones, 1983; Iversen, 1988). When calculating emission/deposition budgets on the regional scale (distances of the order of 1000 km), the factor of major importance seems to be the quality of the meteorological data rather than a high level of sophistication in the chemistry.

Even if a model for oxidised nitrogen necessarily has to include more chemical reactions, attempts have been made to concentrate on the most important processes leading to production of nitrate, and to distinguish between forms of nitrate that have different dry and wet scavenging efficiencies. The model is almost linear, and an allocation of calculated depositions for different emission contributions can be made. The model, a result of extensive collaboration (see Acknowledgements), is operative at the MSC-W of EMEP.

It has been run for the year 1985, from which some results are presented here. Special emphasis is placed on budgets for Poland and Norway.

BASIC MODEL THEORY

A full description of the EMEP NO_x model is given by Eliassen et al. (1988). Here only a short summary is given. Oxidised nitrogen occurs in different forms in the atmosphere. It is mainly emitted as NO, which is quite rapidly oxidised to NO_2 . This NO_x ($\text{NO} + \text{NO}_2$) is then further oxidised to nitrate, which in the model has four different forms, peroxyacetyl nitrate (PAN), HNO_3 , NH_4NO_3 and NO_3^- (particulate nitrate other than ammonium nitrate). The reason for the distinction between all these nitrate compounds is that they have very different properties with regard to dry deposition and precipitation scavenging. Since one of the forms of nitrate is ammonium nitrate, the model must also include emissions of ammonia, which can also combine to form ammonium sulphate. Therefore, the oxidised nitrogen model must include the sulphur model for SO_2 and sulphate. Thus we arrive at a model with 10 chemical components: NO, NO_2 , PAN, HNO_3 , NO_3^- , NH_4NO_3 , NH_3 , $(\text{NH}_4)_2\text{SO}_4$, SO_4^{2-} and SO_2 . When presenting the results, some of these components are grouped together: oxidised nitrogen = $\text{NO}_y = \text{NO}_x + \text{nitrate}$; reduced nitrogen = $\text{N-H}_2 = \text{NH}_3 + \text{ammonium}$; oxidised sulphur = $\text{SO}_x = \text{SO}_2 + \text{sulphate}$.

Figure 1 shows the different chemical pathways in the model. The concentration of O_3 , as well as the radicals OH and CH_3COO_2 , is prescribed from a global two-dimensional model for the zonal average (Isaksen and Hov, 1987).

The model consists of one layer which is assumed to be representative of the daytime mixing layer. A column of air moving with horizontal motion can be

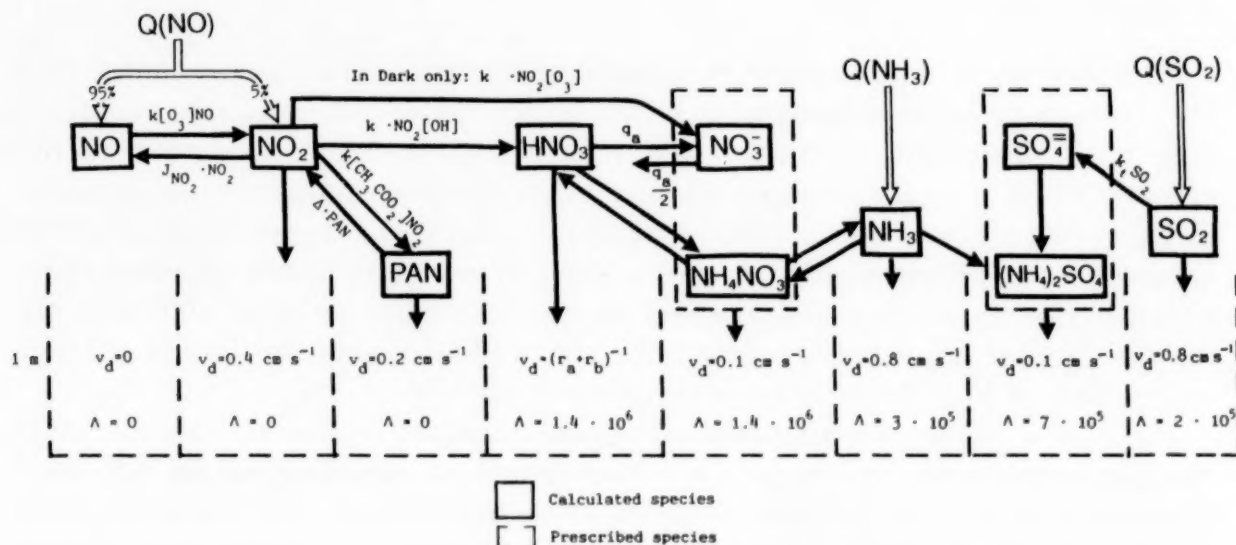


Fig. 1. Flow chart for the chemical pathways in the EMEP NO_x model. Calculated components are those in rectangles. Emissions are signified by Q . Dry deposition velocities at height 1 m and scavenging ratios for each component are given.

considered to conserve its volume, and the equation for the average mass-concentration, q , of a component in the volume can be written:

$$\frac{Dq}{dt} = -kq + Q$$

where Dq/dt is the time derivative of q for an air parcel following the air motion, k is a depletion coefficient and Q is a source/sink term. For a sufficiently small time step $\Delta\tau$, k and Q can be considered constants and the solution is

$$q(\tau + \Delta\tau) = \frac{Q}{k} + \left[q(\tau) - \frac{Q}{k} \right] \exp(-k\Delta\tau)$$

In the present model the coefficients include two effects:

$$k = v_d/h + \Lambda P/h + k_c$$

and

$$Q = Q_0/h + \dot{q}_c$$

Here, h is the height of the air column, v_d the dry deposition velocity, Λ the scavenging ratio, P the precipitation intensity, k_c the chemical depletion coefficient, Q_0 the emission and \dot{q}_c the chemical production rate.

The model is thus Lagrangian, and is in fact a generalised version of the EMEP sulphur model (Eliassen and Saltbones, 1983). The model is receptor oriented. At time t , the model calculates the air concentrations and depositions at a finite number of points (at present 720, among which 108 are measurement sites for EMEP, and the remainder are points in a regular grid). Going backwards in time over 4 days, air parcel trajectories that end at each of these 720 points are calculated every 6 h. These trajectories require knowledge of the

TABLE 1

Meteorological data requirements (frequency: every 6 h, with the exception of local mixing height — every 24 h)

Purpose	Parameter
Trajectories	\vec{V} , horizontal wind
Box height	w , vertical wind
Local mixing height	H
Dry deposition speed	u_* , friction velocity
Dry deposition speed	T_* , flux temperature
Dry deposition speed	T_2 , temperature at 2 m height
Wet deposition	P , precipitation intensity
Chemical coefficients	T , temperature
Chemical coefficients	Rh , relative humidity
Photodissociation	C , cloudiness

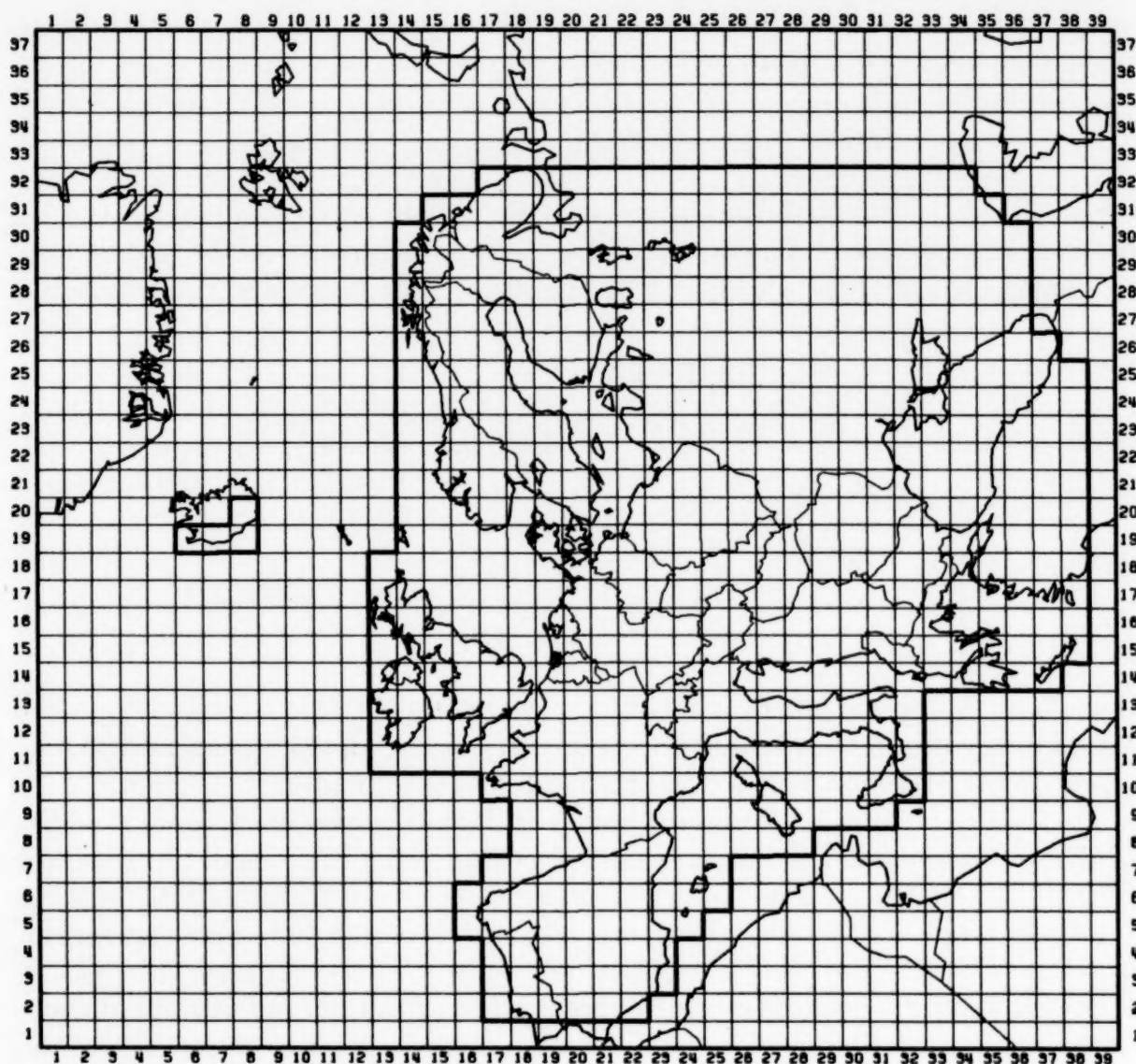


Fig. 2. Area covered by the model calculations. Trajectories are followed over the entire area, but calculations of depositions are only performed for the areas inside the polygons formed by the full, heavy lines.

wind vector as a function of space and time. Furthermore, to calculate all the coefficients required for the determination of the chemistry and wet and dry deposition, a number of meteorological parameters must be known along the trajectories. The dry deposition velocity, v_d , includes the effects of aerodynamic resistance in the turbulent constant flux layer, as well as variations due to surface properties such as land/sea and snowcover. In Fig. 1, the dry deposition velocity is given as its maximum possible value over land without the effect of aerodynamic resistance. Over the sea, negligible dry deposition of NO_2 and peroxyacetyl nitrate is assumed. The air column may change its height, h , as it moves along the trajectory in accordance with the vertical velocity. Every 24 h, when the turbulent boundary layer is assumed to reach its maximum diurnal height, the height of the air column is redefined as the height

of the turbulent mixing layer. In this way the interaction with free tropospheric air is handled; if the box height is higher than the local mixing height, the upper part of the box is assumed to be injected into the free troposphere and is not followed further in the model; if the box height is lower than the mixing layer height, tropospheric air with concentrations equal to the background is mixed into the box.

The meteorological data requirements are summarised in Table 1. These data are analysed in the regular EMEP grid shown in Fig. 2. All meteorological data, except local mixing heights and precipitation over land, are taken from the numerical weather prediction model, which is routinely employed at the Norwegian Meteorological Institute. This system includes a data assimilation system for analysis of meteorological observations (Grønås and Midtbø, 1987). Such a system combines model results with actual observations and has been shown to be an optimal way of making analyses (Hollingsworth, 1987). The mixing heights and the precipitation over land are analysed fields made directly from observations, according to the classical method of Cressman (1959).

CALCULATIONS AND MEASUREMENTS

The EMEP MSC-W NO_x model has been run with actual meteorological data for all of 1985. Data for emissions of SO_2 and NO_x were taken, when available, from official data submitted to the ECE secretariat in Geneva. Otherwise, emissions have been estimated by MSC-W and the Chemical Coordinating Centre (CCC, The Norwegian Institute for Air Research, NILU) in cooperation. Emission estimates for NH_3 were those of Buijsman et al. (1985) multiplied by 1.2 according to recommendations given by the authors of that report. Table 2 shows the emissions used for 1985 for Europe, Poland and Norway. Emissions for the two German republics are included in order to demonstrate the striking difference between Western and Eastern European emission of SO_2 and NO_x . MSC-W acknowledges the valuable contribution from the Polish coordinating centre of the EMEP programme, which submitted emission data for sulphur in Poland for the EMEP grid mesh (EMEP/POL — Rep. 1/1987).

TABLE 2

Emissions used, 1985 (10^3 t year^{-1} as S or N)

	SO_2	NO_x	NH_3
Europe	22065	5936	7558
Poland	2150	457	394
Norway	50	68	39
Federal Republic of Germany	1200	882	361
German Democratic Republic	2500	291	200

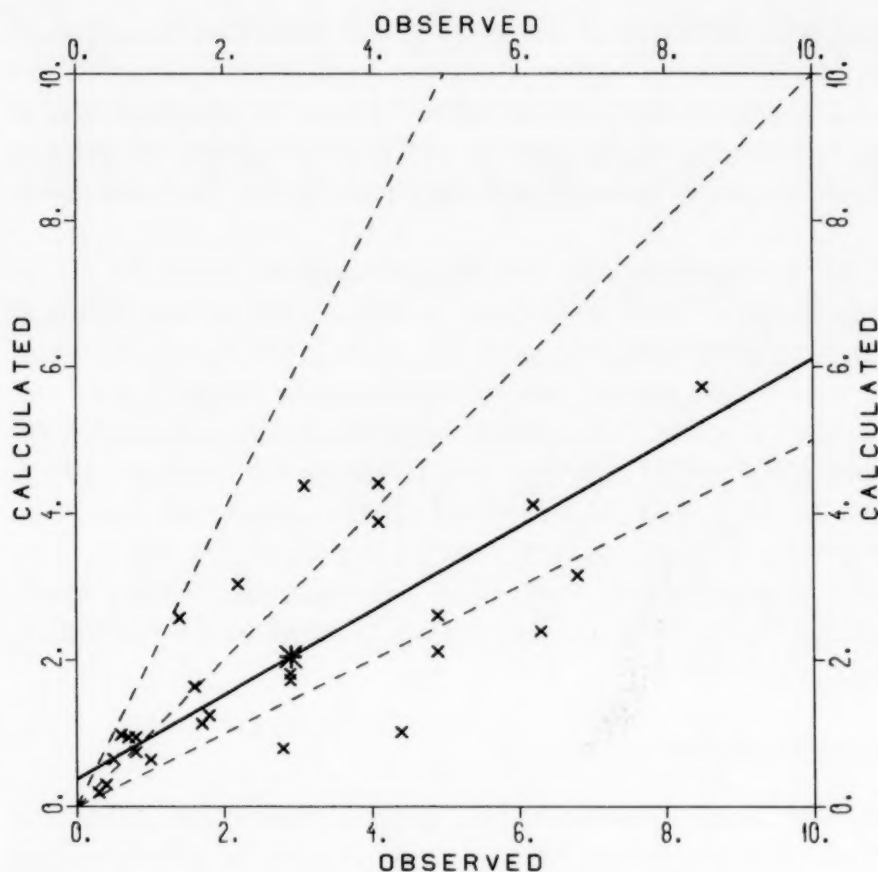


Fig. 3. Calculated versus observed concentrations of NO_2 in air ($\mu\text{g Nm}^{-3}$). The heavy line shows the direction along which the variance is maximum (first principal component). Lines for perfect agreement and disagreement within a factor of two are shown as broken lines.

Figure 3 shows a scatter plot for measured and calculated airborne nitrogen dioxide, NO_2 , at EMEP stations for 1985. The correspondence is reasonably good, however the model seems to underestimate the concentrations. On the other hand, a pilot study under the Nordic Council of Ministers has revealed large uncertainties in the measurements of low NO_2 concentrations (not yet published). The intercalibration between Nordic laboratories revealed a spread of up to a factor of two. This must be borne in mind when interpreting Fig. 3. There is good correspondence between measured and calculated concentrations at most of the stations in the Federal Republic of Germany, and also at Norwegian and Swedish stations. However, the model underestimates considerably the concentrations at Polish stations. Similar scatter diagrams for sulphur dioxide and particulate sulphate (not shown here) show much smaller discrepancies.

Figure 4 shows a scatter plot for nitrate in precipitation (observed versus calculated). Calculated values are represented by intervals denoted by vertical lines. The lower point of a line is the directly obtained model estimate, while the upper point is derived by adding the contribution from dry deposition on days with precipitation ("wet days"). The optimal estimate should be

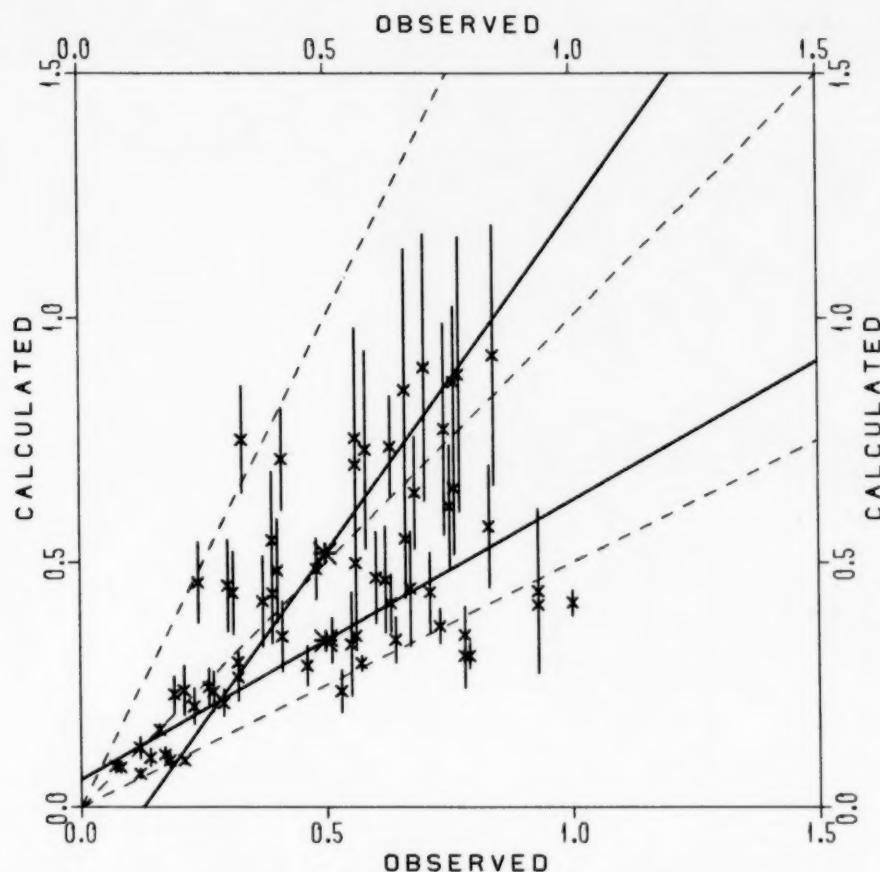


Fig. 4. Calculated versus observed concentrations of nitrate in precipitation (mg N l^{-1}). Calculated values are denoted by intervals in which the lower bound is found by taking into account only wet deposition, while the upper bound is found by adding the contribution from dry deposition.

somewhere in this interval. It can be seen that the concentrations are much better reproduced when the dry deposition contribution is added. The quality of the nitrate calculations is then reasonably good. Figure 5 shows a similar diagram for ammonium in precipitation. There is a significant general underestimation of the observed values. The main reason for this underestimation is probably the location of the measurement stations in rural areas where the emissions of NH_3 are large. Thus the EMEP measurements are not representative of grid volume averages in this case.

The quality of the output from long-range transport models depends on the accuracy of the emission data, the quality of the meteorological data and the correctness of the parameterisation of removal processes. The meteorological data is probably the strongest link in this chain. Official emission data are missing for several European countries, and only a few countries have given emission data in gridded form. There are also reasons to believe that there are considerable emissions of NO_x from shipping traffic. These have not yet been included in the calculations, and may explain the underestimated concentrations of NO_2 and nitrate at certain locations.

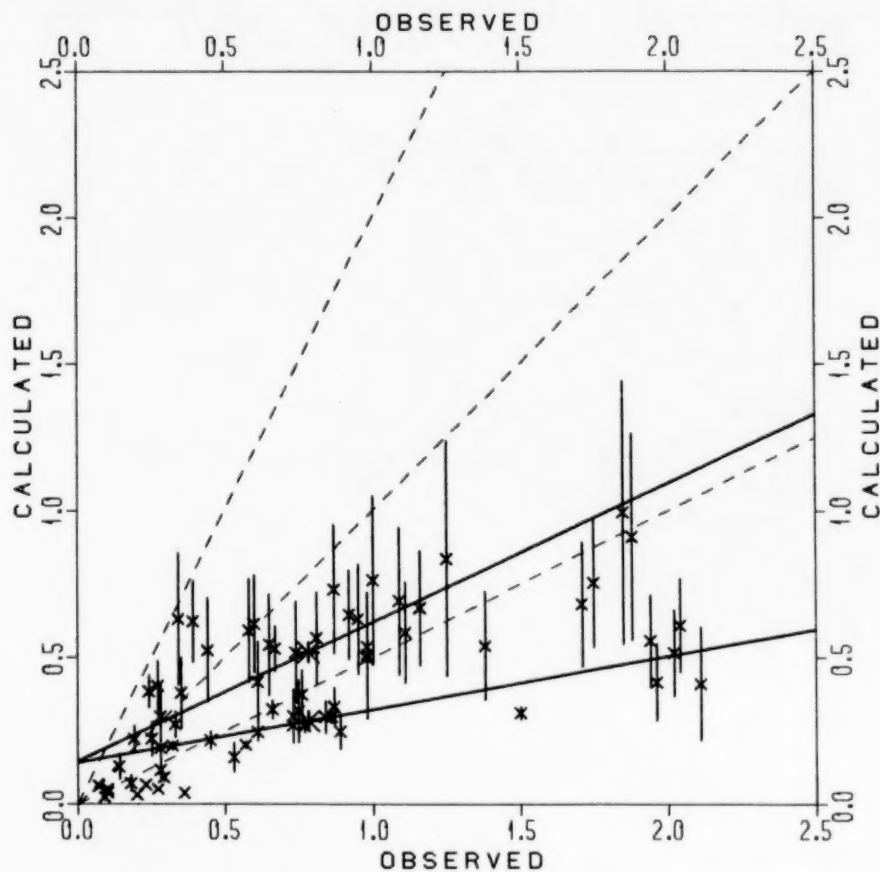


Fig. 5. As for Fig. 4, but for ammonium in precipitation.

SOME RESULTS

The model calculates budgets for all airborne and deposited components included in the model. Figure 6 shows calculated deposition maps for SO_x and NO_y in Europe. The maximum depositions are estimated to be in Central Europe for both components. However, the area with maximum deposition is displaced towards the west for NO_y as compared with SO_x . For all countries of Europe, the contributions from emissions from all European countries are estimated, in addition to contributions from indeterminate sources. Emitter/receiver matrices for deposited oxidised sulphur, oxidised nitrogen and reduced nitrogen have been reported by Eliassen et al. (1988). Here, we shall only present budgets for Poland (Table 3), Norway (Table 4) and Europe (Table 5). Poland is a net exporter of all three species. Since the deposition of oxidised nitrogen is slow close to the source, Poland exports a larger part of its NO_x emissions than its SO_2 or NH_3 emissions. This is because a large part exists as NO or NO_2 until the air moves out of Poland. More than half of the SO_2 and NH_3 emissions are deposited within Poland, while more than 70% of the NO_y

Fig. 6. Calculated total (wet + dry) deposition in Europe. (a) Oxidised sulphur (g Sm^{-2}); (b) Oxidised nitrogen (g Nm^{-2}).

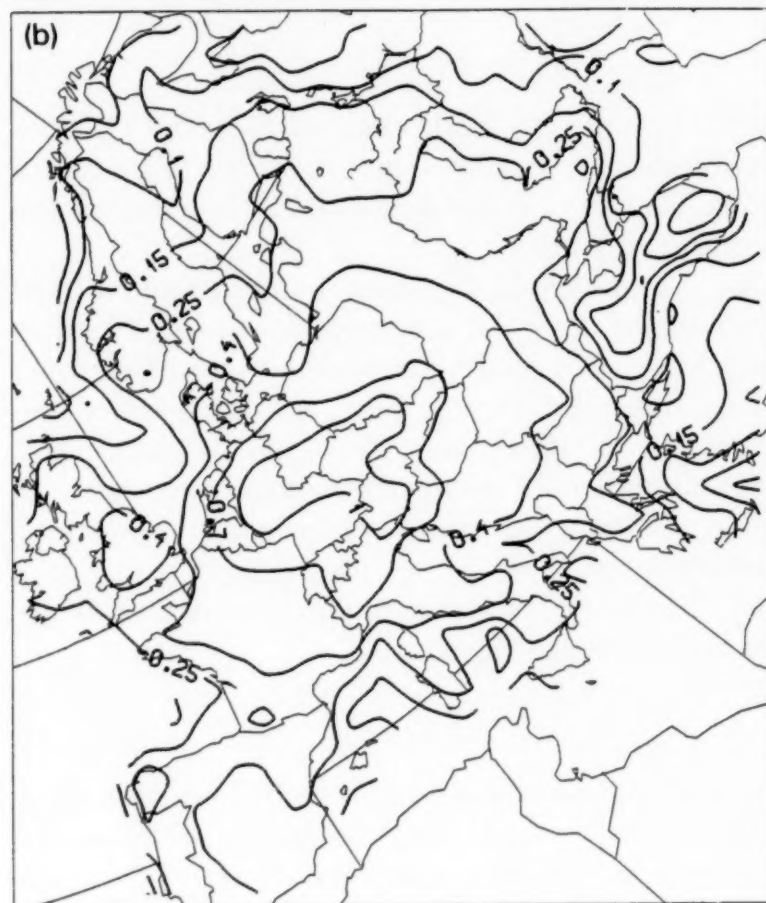
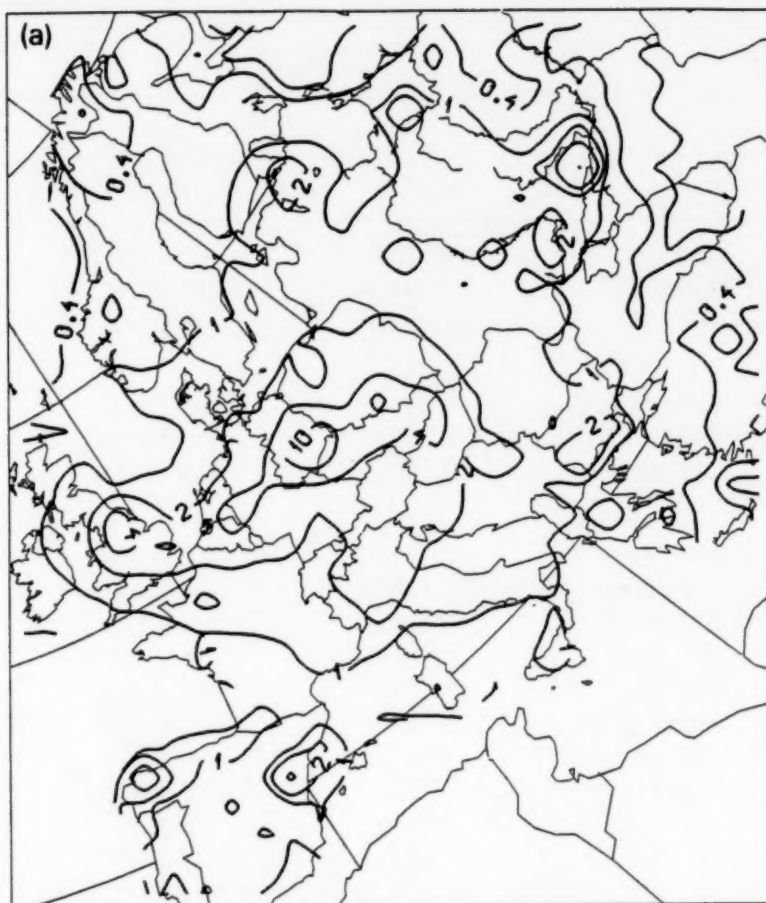


TABLE 3

Emission-deposition budgets for Poland, 1985 (results for SO_x are from the MSC-W sulphur model) (10^3 t year^{-1} as S or N)

	SO_x	NO_y	NH_3
Emission	2150 (100) ^a	457 (100)	394 (100)
Deposition	1145 (53.3)	203 (44.4)	200 (50.8)
Net export	1005 (46.7)	254 (55.6)	194 (49.2)
From Poland to:			
Poland	650 (30.2)	54 (11.8)	115 (29.4)
Rest of Europe	613 (28.5)	191 (41.8)	130 (33.0)
Indeterminate ^b	887 (41.3)	212 (46.4)	149 (37.6)
To Poland from:			
All sources	1145 (100)	203 (100)	200 (100)
Rest of Europe	444 (38.8)	141 (69.5)	84 (42.0)
Poland	650 (56.8)	54 (26.7)	115 (57.5)
German Democratic Republic	189 (16.5)	26 (12.8)	16 (8.0)
Federal Republic of Germany	36 (3.1)	39 (19.2)	11 (5.5)
Czechoslovakia	109 (9.5)	26 (12.8)	10 (5.0)
Hungary	29 (2.5)	4 (2.0)	4 (2.0)
Soviet Union	18 (1.6)	4 (2.0)	16 (8.0)
United Kingdom	15 (1.3)	8 (3.9)	3 (1.5)
Indeterminate	51 (4.5)	8 (3.9)	1 (0.5)

^aPercentages in parentheses.

^bIncludes areas outside Europe.

deposition originates from outside Poland. It can also be seen from both Tables 3 and 4 that Eastern European countries are more important contributors of sulphur than of oxidised nitrogen. This is well demonstrated by comparing the contributions from the two German republics.

Table 4 shows that Norway is a net importer of oxidised sulphur and reduced nitrogen, while it is a net exporter of oxidised nitrogen. However, Norway receives more oxidised nitrogen from, than it delivers to, the rest of Europe. Being a remote country with a long coast facing west, a large part of the calculated depositions in Norway is indeterminate. This is especially important for oxidised sulphur. Indeterminate in this connection means that it is not possible to attribute the depositions to known emissions by means of 4-day trajectories for the boundary layer.

In Table 5 the Norwegian and Polish contributions to depositions in Europe are compared with the total estimated depositions.

CONCLUSIONS

The agreement between measured and observed concentrations of NO_2 , and nitrate in precipitation, is sufficient to conclude that the model includes the essential features necessary to describe regional scale dispersion of oxidised nitrogen in the atmospheric boundary layer. The success of the model is to a

TABLE 4

Emission-deposition budgets for Norway, 1985 (results for SO_x are from the MSC-W sulphur model) (10^3 t year^{-1} as S or N)

	SO_x	NO_y	NH_3
Emission	50 (100) ^a	68 (100)	34 (100)
Deposition	190 (380.0)	62 (91.2)	43 (126.5)
Net export	- 140 (- 280.0)	6 (8.8)	- 9 (- 26.5)
From Norway to:			
Norway	9 (18.0)	6 (8.8)	10 (29.4)
Rest of Europe	5 (10.0)	13 (19.1)	5 (14.7)
Indeterminate ^b	36 (72.0)	49 (72.1)	19 (55.9)
To Norway from:			
All sources	190 (100)	62 (100)	43 (100)
Rest of Europe	80 (42.1)	43 (69.4)	31 (72.1)
Norway	9 (4.7)	6 (9.7)	10 (23.8)
Indeterminate	101 (53.2)	13 (21.0)	1 (2.4)
United Kingdom	20 (10.5)	12 (19.4)	7 (16.3)
Soviet Union	11 (5.8)	3 (4.8)	4 (9.3)
German Democratic Republic	11 (5.8)	2 (3.2)	1 (2.4)
Federal Republic of Germany	8 (4.2)	7 (11.3)	2 (4.8)
Poland	7 (3.6)	3 (4.8)	2 (4.8)
Sweden	4 (2.1)	4 (6.6)	2 (4.8)

^aPercentages in parentheses.

^bIncludes areas outside Europe.

large extent a consequence of the availability of meteorological data of good quality. However, there are some regions, for example Poland, where calculations underestimate observations. The concentrations of ammonium in precipitation are even more underestimated.

The results indicate that, while Eastern European countries are responsible for much of the deposited sulphur in Europe, Western European countries are more responsible for oxidised nitrogen deposition. The deposition patterns are such that small countries export relatively more oxidised nitrogen than sulphur, while their export of reduced nitrogen is similar to that of sulphur.

The calculations reveal large differences between Poland and Norway with respect to pollution burden, even if one takes into account the large local variation within Norway. Poland receives five times as much SO_x and NH_3 as Norway, while the factor is about 3.5 for NO_y . (The two countries are almost equal in area.) It is because of the difference in the buffer capacities of the soils that Norway probably has a greater acidification problem than Poland.

ACKNOWLEDGEMENTS

The EMEP/MS-CW NO_x model was developed with contributions from

TABLE 5

Depositions in Europe from emissions of the different countries of Europe, 1985. Data for SO_x are from the MSC-W sulphur model (10^3 t year^{-1} as S or N)

To Europe from	SO_x	NO_y	NH_3
All sources (total deposition)	12268 (100) ^a	2869 (100)	3594 (100)
Poland	1263 (10.3)	245 (8.5)	245 (6.8)
Norway	14 (0.1)	19 (0.7)	15 (0.4)
Soviet Union	2217 (18.0)	283 (9.9)	1160 (32.2)
Indeterminate	1489 (13.0)	363 (12.7)	21 (0.6)
German Democratic Republic	1479 (12.1)	166 (5.8)	123 (3.4)
United Kingdom	767 (6.3)	202 (7.0)	181 (5.0)
Czechoslovakia	888 (7.2)	179 (6.2)	94 (2.6)
Federal Republic of Germany	704 (5.7)	453 (15.8)	202 (5.6)
Italy	544 (4.4)	163 (5.7)	151 (4.2)
Spain	534 (4.4)	68 (2.4)	83 (2.3)
France	515 (4.2)	243 (8.5)	397 (11.0)
Hungary	461 (3.8)	51 (1.8)	78 (2.2)
Yugoslavia	314 (2.6)	24 (0.8)	92 (2.6)
Bulgaria	206 (1.7)	9 (0.3)	49 (1.4)
Belgium	141 (1.1)	66 (2.3)	50 (1.4)
Denmark	80 (0.7)	33 (1.2)	56 (1.6)
Finland	94 (0.8)	32 (1.1)	23 (0.6)
The Netherlands	76 (0.6)	84 (2.9)	85 (2.4)
Sweden	68 (0.6)	40 (1.4)	27 (0.8)

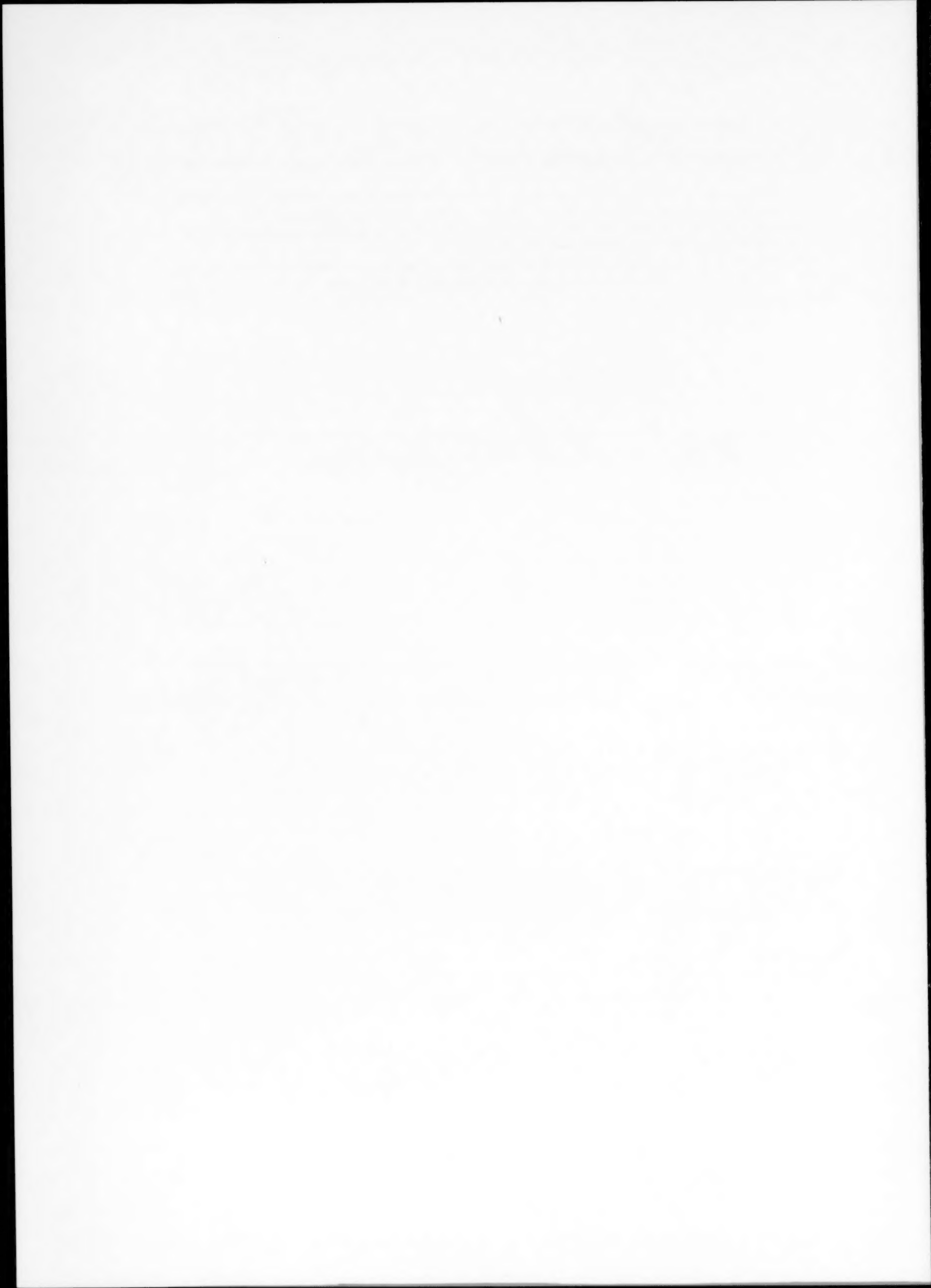
^aPercentages in parentheses.

Anton Eliassen and Trond Iversen from MSC-W, Øystein Hov from the Norwegian Institute for Air Research (NILU) and David Simpson from Warren Springs Laboratory, U.K. Jørgen Saltbones, MSC-W, is responsible for the emission surveys and the sulphur calculations presented here. The preparation of meteorological data from the numerical weather prediction model was by Thor Erik Nordeng of the Norwegian Meteorological Institute. The development of the EMEP NO_x model has received funding through EMEP, the Nordic Council of Ministers and the Government of Canada.

REFERENCES

- Buijsman, E., J.F.M. Maas and W.A.H. Asman, 1985. Ammonia emissions in Europe. Institute voor Meteorologie en Ocenaografie, Rijksuniversiteit, Utrecht, Rep. IMOU-R-85-2.
- Cressman, G.P., 1959. An operational objective analysis system. *Mon. Weather Rev.*, 87: 367-374.
- Eliassen, A., 1978. The OECD study of long range transport of air pollutants: long range transport modelling. *Atmos. Environ.*, 12: 479-487.
- Eliassen, A. and J. Saltbones, 1983. Modelling of long-range transport of sulphur over Europe: a two-year model run and some model experiments. *Atmos. Environ.*, 17: 1457-1473.
- Eliassen, A., Ø. Hov, T. Iversen, J. Saltbones and D. Simpson, 1988. Estimates of airborne trans-boundary transport of sulphur and nitrogen over Europe. EMEP/MSC-W Rep. 1/88.
- Grønås, S. and K.H. Midtbø, 1987. Operational multivariate analyses by successive corrections.

- Collection of Papers presented at the WMO/IUGG NWP Symposium, Tokyo, 4-8 August 1986, pp. 61-74.
- Hollingsworth, A., 1987. Objective analysis for numerical weather prediction. Collection of Papers presented at the WMO/IUGG NWP Symposium, Tokyo, 4-8 August 1986, pp. 11-59.
- Isaksen, I.S.A. and Ø. Hov, 1987. Calculations of trends in the tropospheric concentration of O_3 , OH, CO, CH_4 and NO_x . *Tellus*, 39B: 271-285.
- Iversen, T., 1989. Numerical modelling of the long-range atmospheric transport of sulphur dioxide and particulate sulphate to the Arctic. *Atmos. Environ.*, 23: 2571-2595.



THE ROLE OF NITROGEN OXIDES IN THE LONG-RANGE TRANSPORT OF PHOTOCHEMICAL OXIDANTS*

ØYSTEIN HOV

Norwegian Institute for Air Research, P.O. Box 64, N-2001 Lillestrøm (Norway)

ABSTRACT

Ozone episodes in the atmospheric boundary layer over Europe are superimposed on a background level which is slowly increasing. The change in the background concentration is probably controlled by changes in the emissions of nitrogen oxides (NO_x). It is likely that a further increase in the emissions of NO_x in Europe and elsewhere in the Northern Hemisphere will contribute to a continued rise in free tropospheric ozone, while the occurrence of ozone episodes in the boundary layer may not change much.

Nitrate derived from the emissions of NO_x contributes significantly to acid deposition in Europe and elsewhere. Integrated over 1 year and over all of Europe, there is probably an almost linear relationship between a change in NO_x emissions and the corresponding change in nitrate deposition.

A reduction in the emissions of NO_x in a photochemical episode in Europe could lead to only a slight decrease in the concentration of hydroxyl radical (OH) and ozone, while there might be a marked increase in hydrogen peroxide. The conversion of NO_x to nitrate would become slightly slower, while the conversion of SO_2 to sulphate would remain fairly unchanged. The atmospheric lifetime of NO_x and sulphur species could remain the same or increase slightly.

In clean air, a downward trend in the emission of NO_x (a few percent per year) is shown in model calculations to cause a reduction in the background concentration of ozone and OH, while H_2O_2 increases. This means that the gas-phase conversion of SO_2 and NO_x , through the reaction with OH, to sulphate and nitrate will become less efficient. In addition, the dark reaction converting NO_2 to the NO_3 radical and further to nitrate through reaction with ozone, would become slower, while the wet-phase oxidation of SO_2 to sulphate would become more efficient. This means that reduced emissions of NO_x would give rise to a more than proportional reduction in nitrate formation, while the efficiency of sulphate formation could increase. For the distribution of acid deposition this would imply an increase in the lifetime for sulphur compounds and a decrease in the lifetime for NO_x compounds.

* Full paper published as Norwegian Institute for Air Research Report 12/88.



METAL SOLUBILITY AND PATHWAYS IN ACIDIFIED FOREST ECOSYSTEMS OF SOUTH SWEDEN

DAN BERGGREN, BO BERGKVIST, URSULA FALKENGREN-GRERUP, LENNART FOLKESON and GERMUND TYLER*

Department of Plant Ecology, Soil Ecology Group, University of Lund, Ö. Vallgatan 14, S-223 61 Lund (Sweden)

ABSTRACT

Considerable decreases in pH and base saturation have occurred during the last decades both in the upper and in the lower horizons of natural and seminatural soils of northwestern Europe, and are particularly well documented in southern Scandinavia. Increased fluxes of strong mineral acids, partly or mainly derived from atmospheric deposition, seem to be the main reason for these changes. The solubility of aluminium, base cations, manganese, cadmium, zinc and nickel has increased as a consequence, and large areas of forest soils now have acidity conditions such that any additional input of strong mineral acids causes a rapid increase in the release rates of these elements. Soil acidification and metal fluxes differ between tree species (spruce, beech and birch). The effect of soluble humic matter on metal solubility is discussed, as is the importance of metal speciation to the flux rates of elements in forest ecosystems.

INTRODUCTION

Until recently, soils were considered quite resistant to acidification or other adverse effects of the deposition of acidic pollutants. The basis of this resistance would be, for example, mineral weathering and a large cation exchange capacity, properties easily buffering the possible adverse influence of acidic deposition. During the last few years, however, considerable evidence has been presented in support of the view that soils are far more sensitive than originally thought. The aims of this study are to review recent and current research on soil acidification — metal solubility problems in south Sweden, a region exposed to deposition of mainly long-distance-transported acidic pollutants.

SOIL ACIDIFICATION

Several studies from south Scandinavia have shown that forest soils have become, on average, 0.5 – 1.0 pH units lower during the course of a few decades (for a review of the literature see Berdén et al., 1987). This change has occurred

* Author to whom correspondence should be addressed.

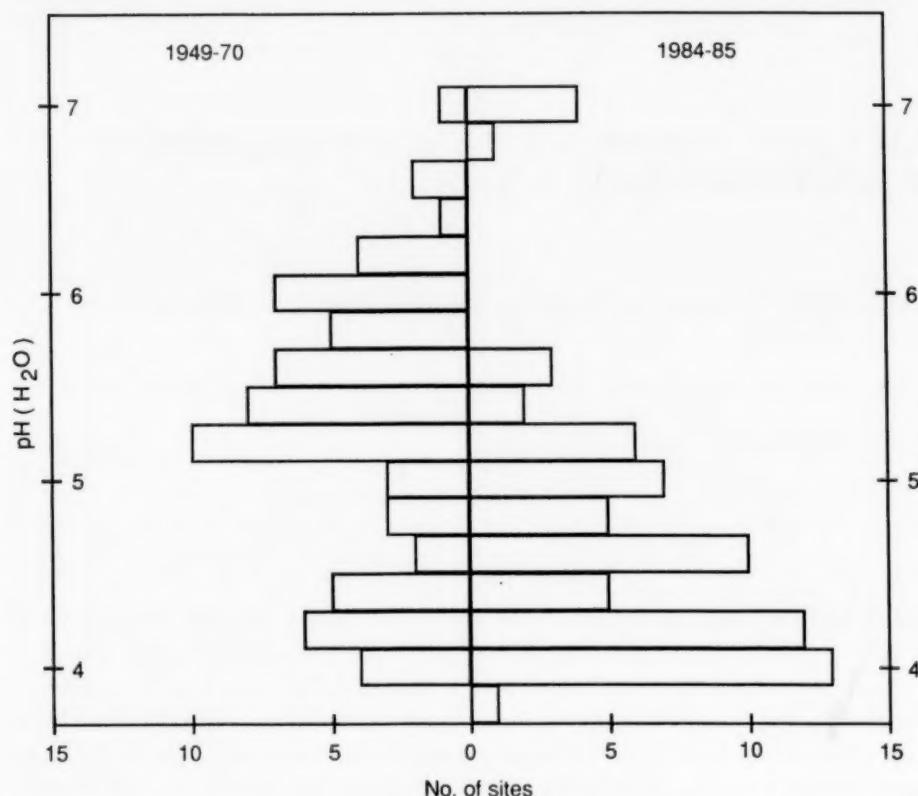


Fig. 1. The distribution of soil pH (H_2O) at 68 beech forest sites in Scania (S. Sweden) studied in 1949-70 and 1984-85. Samples were taken from the A horizon (0-5 or 0-10 cm) using the same methods of sampling and analysis on both occasions.

in the deeper horizons of all natural and seminatural soils, as well as in the humus layer of forest and heathland soils, except possibly in originally very acidic mor (0) horizons (Falkengren-Grerup, 1987; Falkengren-Grerup et al., 1987).

The pH decrease is particularly great in the light-textured, well-drained Dystric Cambisols of south Sweden, situated just outside the main source area of atmospheric pollutants in Europe and subjected to a considerable import of unneutralized strong mineral acids with the prevailing south-southwesterly air currents. No pH changes were found over 30-60 years in the north of Sweden, whereas slight pH decreases were measured in the central parts of the country (Tamm and Hallbäcken, 1988; Jacks et al., 1989). Norway is also exposed to the deposition of acidifying substances and pH decreases of 0.3-0.9 units were recorded in podzols of a mountainous area of south Norway over a period of 40 years (Dahl, 1988). While 75% of the beech forests studied in south Sweden had a pH (H_2O) > 5.0 in the humus layer 15-35 years ago, only 25% exceeded this level in 1984-1985 (Fig. 1). The only exceptions to these trends towards higher soil acidity were found in a few stands influenced by seeping groundwater.

Part of the pH decrease will be due to increased forest primary productivity, caused by improved stand management, but possibly also by increased nitrogen deposition. Higher production increases the plant uptake of base cations,

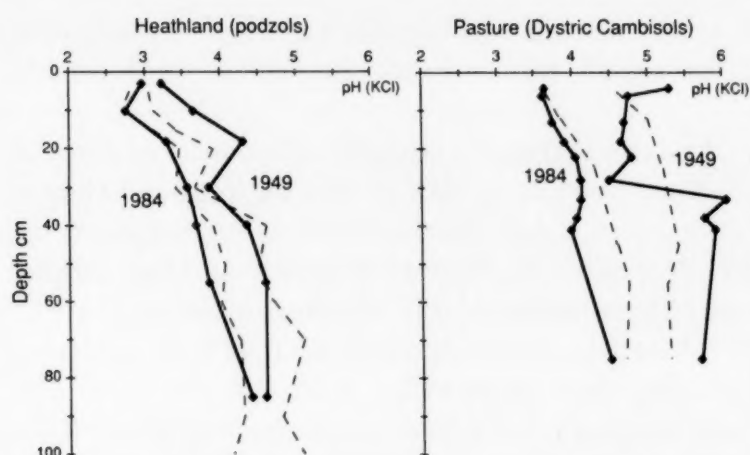


Fig. 2. The pH (M KCl) at different soil depths below a *Calluna* heathland on a podzolic soil (left) and below a pasture (right) with scattered *Juniperus* on a Dystric Cambisol, measured in 1949 and 1984 (solid lines). Also indicated are the pH (M KCl) curves (dashed lines) for a number of similar soils under forest, studied in the same years.

causing a net flux of hydrogen ions to the soil. However, the pH decrease is much greater than expected from the productivity increase alone. It is also considerable in heathlands, where the net accumulation of base cations in the biomass is almost negligible. A *Calluna* heathland soil showed pH decreases over a 35 year period that were of the same magnitude and pattern as in forest podzols, i.e. with consistent decreases down to at least 1 m depth. A *Juniper* pasture had changed in a similar way as the Dystric Cambisols, showing large pH decreases in all horizons (Fig. 2).

A close consideration of old and new pH data from forest soils in one thoroughly studied area (Tönnersjöheden in Halland) has shown that pH

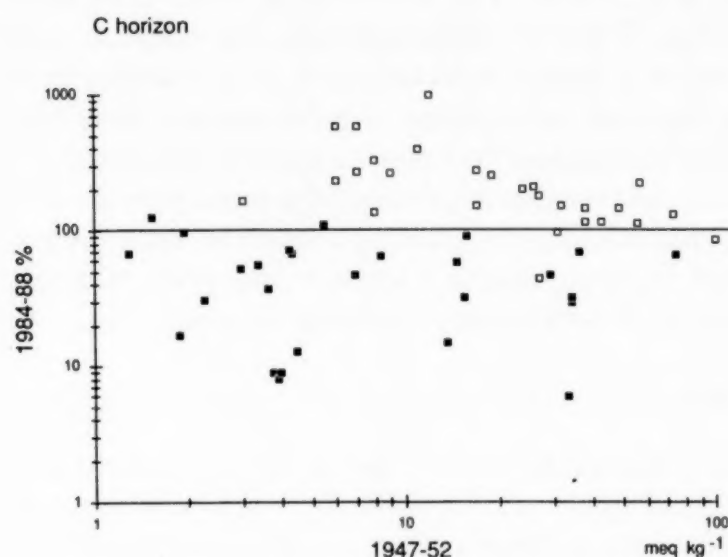


Fig. 3. Exchangeable base cations ($\text{Na} + \text{K} + \text{Ca} + \text{Mg}$) and Al in 1984–88 as a percentage of that in 1947–52 in the upper C horizons (70–100 cm depth) of deciduous forest soils in south Sweden. Air-dried, old and recently sampled soil was extracted simultaneously using M $\text{NH}_4\text{OCOCH}_3$ solution of pH 4.8. (■) Base cations; (□) Al.

changes during the last 50 years in the deeper soil horizons are not explainable by ageing of the stands and increased mineral accumulation in biomass (Hallbäcken and Tamm, 1986).

From the current variability of base saturation and pH in topsoils of forests in south Sweden [typical mor (0) horizons excluded], it may be deduced that a pH decrease of 0.7–0.8 units is related to a decrease of the base saturation by a factor of two (Tyler et al., 1987). Repeated studies of 10 forest and heathland soils (in 1949 and 1984) confirmed this relationship (Falkengren-Grerup et al., 1987). During these 35 years, 30–70% of the exchangeable pool of base cations, down to a depth of ~1 m, had disappeared in parallel with the recorded pH decrease. The lowering of the base cation pool was even more pronounced in the upper part of the morphological C horizon of another 19 beech and oak stands studied in 1948 and 1988. Half the number of sites had lost more than 50% of their base cation pools at this soil depth during four decades (Fig. 3). To a great extent they had been replaced by aluminium.

The exhaustion of exchangeable or easily soluble base cation (and possibly other mineral) pools is of great concern. The 'consuming' processes, including increased leaching, exceed the 'supporting' ones. It is evident that mineral weathering is incapable of keeping pace with the losses, and that soils, when acidified, may become deficient in bioavailable nutrients.

It is difficult to predict to what extent these changes will be reversible. Most forest soils in Scandinavia are derived from silicate rocks (granite, gneiss) and probably have a low weathering capacity. Experimental or empirical data seem to indicate that the weathering rate of feldspars does not increase on acidification (Helgeson et al., 1984; Fölster, 1985), though contrary information is also found (e.g., Bache, 1980). Recent field measurements of Sr isotope ratios indicate that the present weathering rate cannot compensate for current losses of exchangeable cations (Åberg et al., 1989). The weathering rate in an acid spruce forest soil in south Sweden (Värsjö) was much too low (Olsson and Melkerud, 1989) to compensate for the losses from this soil as quantified in a budget study (Bergkvist, 1987b). Annual net release of base cations from the rhizosphere with percolating soil solution was 10 times as high as the amounts added to the exchangeable soil store by weathering during the same period. The proportion of dark minerals (e.g. biotite, olivine), though small in most forest soils, is of importance. Soil acidification might decrease the pool of such minerals by increased weathering and subsequent leaching losses.

METAL SOLUBILITY AND SPECIATION

Decreases in pH and depletion of the exchangeable pools of base cations are not the only consequences of soil acidification. The solubility of Al and several other metals (e.g., Mn, Cd, Zn, Ni) also increases. The amount and quality of soil minerals and humus constituents, and the activity of soil organisms, make release rates difficult to predict.

Different buffer systems act to neutralize protons deposited on the soil or

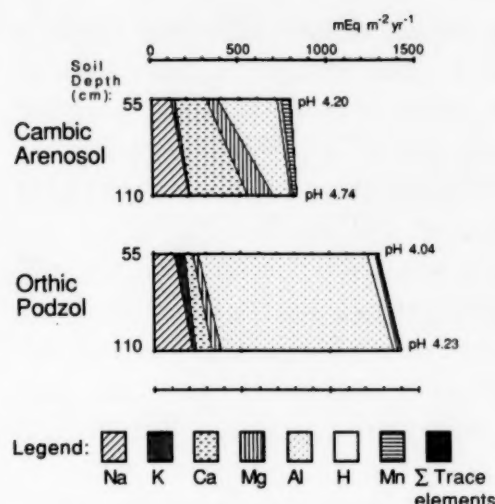


Fig. 4. Annual fluxes of elements (3-year means) through the upper C horizons and mean pH in the soil solution of a Cambic Arenosol (Sjöbo) and an Orthic Podzol (Horröd) underlying spruce forest in south Sweden. The Cambic Arenosol is within the cation exchange buffer range ($\text{pH} > 4.2$) and the Orthic Podzol within the aluminium buffer range ($\text{pH} 4.2\text{--}2.8$) according to Ulrich (1983). Soil monoliths from the upper C horizons were contained in plexiglass percolation lysimeters (see Bergkvist, 1987b) and placed in a cold laboratory ($+6^\circ\text{C}$). They were irrigated with field-sampled B horizon lysimeter soil solutions twice a week for 3 years.

produced within it. In soils within or above the cation exchange buffer range ($\text{pH} > 4.2$), increased soil acidity leads to the liberation and leaching of Ca and Mg, while the leaching of Al is the buffer reaction in soils within the aluminium buffer range ($\text{pH} 4.2\text{--}2.8$) (Ulrich, 1983). This is demonstrated in Fig. 4, which compares metal fluxes through the upper C horizon of an Orthic Podzol and a Cambic Arenosol in south Sweden. In the Cambic Arenosol the buffering action to a large extent resulted in the release of Ca and Mg. In the Orthic Podzol a significant release of Al occurred.

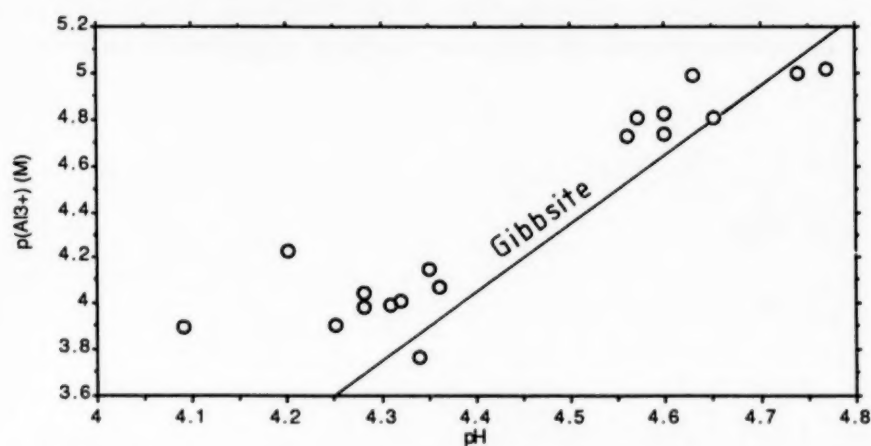


Fig. 5. The relationship between $\text{p}(\text{Al}^{3+})$ (negative logarithm of the Al^{3+} activity) and pH in soil solutions from 50 cm depth in beech, birch, and spruce stands at two different sites in south Sweden. The Al^{3+} activity was obtained using the ion exchange column procedure proposed by Driscoll (1984), followed by thermodynamic calculations (LaZerte, 1984). Solubility lines for natural gibbsite were calculated using the solubility constant of Seip et al. (1984), recalculated to 8°C .

The Al^{3+} activity in soil solutions from 50 cm depth at two different sites in Scania, south Sweden, representing both podzols and Dystric Cambisols, is illustrated in Fig. 5. At $\text{pH} > 4.2$, the points lie close to the solubility line for gibbsite. This is in accordance with results from the ALBIOS project, where most B and C horizon soil solutions exhibited Al^{3+} activities consistent with an aluminium trihydroxide solubility model (Cronan et al., 1987).

Most forest soils of south Scandinavia and northwest Europe have a pH within, or close to, the interval where any additional pH decrease is likely to cause an increase in the solubility of Al, and also of other elements, such as Cd. Within the soil solution pH range of 4.0–4.5, a pH decrease of 0.1–0.2 units may result in a two- to three-fold increase in the solution concentration of Cd (Bergkvist, 1987a). Since the Cd fraction associated with the solid phase is mainly exchangeable (Bergkvist, unpublished data) it seems probable that $\text{Al}^{3+}/\text{Cd}^{2+}$ exchange on negatively charged soil colloids is important for the control of Cd transport in B horizons of acid forest soils.

The high release of inorganic Al from the B horizon, being highly pH-dependent, seems to be a recent phenomenon. It is consistent with the known decreases in soil pH since ~1950. Strong mineral acids (H_2SO_4 , HNO_3 , HCl) are the driving forces of this release from the deeper horizons rather than natural organic acids. The spruce and beech forests in many areas exposed to considerable dry deposition of acids from adjacent or remote sources now have a negative budget of Al, Zn and Cd.

High concentrations of humic matter, as in the soil solution of the E horizon of podzols, may greatly modify the solubility pattern. In a study on the leaching of metals from the E horizon of a spruce forest soil (Tyler, 1981) it was concluded that elements such as Al, Fe, Pb, Cu, Cr and V may be leached from the topsoil to the B horizon under conditions favouring leaching of soluble humic substances, i.e. during periods of comparatively high soil temperature and moisture. Metals with a larger fraction present in a readily exchangeable form (Na, Mg, Ca, Zn, Cd) were more susceptible to minor pH changes. The correlation between the concentrations of organic matter and Pb in the soil

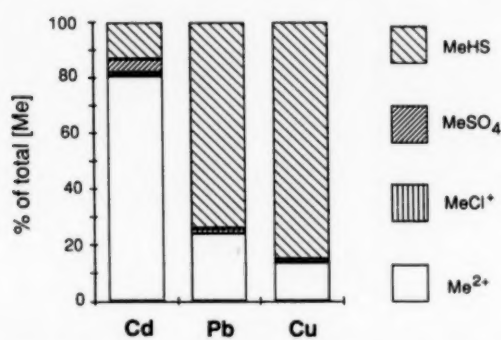


Fig. 6. The relative speciation of Cd, Pb and Cu in a soil solution collected from a Dystric Cambisol at a depth of 15 cm. The speciation was obtained using an equilibrium dialysis method (Berggren, 1989), together with thermodynamic calculations. Equilibrium constants were adopted from Lindsay (1979). Total concentrations of Cd, Pb, and Cu were 19.9, 171, and 769 nM, respectively, DOC 9.8 mg l⁻¹ and pH 4.5.

TABLE 1

The speciation of Cd in some forest soil solutions using Donnan dialysis. A strong cation exchange membrane (R-1010, Research Corporation) was inserted into a small dialysis cell (Risinger et al., 1989) installed in a flow-injection system with an electrochemical cell for detection of Cd^{2+} by differential-pulse anodic stripping voltammetry (Yang et al., 1987). Samples were spiked with $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, adjusted for ionic strength (0.10 M NaNO_3) and pumped through the cell on one side of the membrane. A receiver solution of identical ionic strength (99.5 mM NaNO_3 , $0.5\text{ mM CH}_3\text{COONa}$, pH 4.33) was present on the opposite side and 'stopflow' was used. After equilibration of the dialysis cell ($\sim 30\text{ min}$), the receiver solution was pumped through the electrochemical cell. Since the membrane is negatively charged, only positively charged Cd species will pass through. Mainly Cd^{2+} was detected on the receiver side^a. The analytical system has been tested using well defined ligands (citric acid and nitrilotriacetic acid) and good results have been obtained, provided the pH in the receiver and sample solutions is the same (Berggren, unpublished).

Soil type	Sampling depth (cm)	$\text{Cd}_{\text{added}}^{\text{b}}$ (μM)	$\text{Cd}_{\text{inorg}}^{\text{a}}$ (%)	Cd_{org} (%)	DOC^{c} (mg l^{-1})	pH
Podzol	15	1.00	52	48	269	4.22
Podzol	15	0.50	54	46	269	4.23
Dystric Cambisol	15	0.50	90	10	10	4.15
Dystric Cambisol	50	0.25	100	0	2.9	4.56

^a $\text{Cd}_{\text{inorg}} = [\text{Cd}^{2+}] + [\text{CdNO}_3^+]$. Since 0.10 M NO_3^- was added to samples and standards, some CdNO_3^+ complexes were also formed. $[\text{CdNO}_3^+]/[\text{Cd}_{\text{inorg}}]$ was in all cases 0.07, if equilibrium constants from Lindsay (1979) were used in the calculations. Ninety-three percent of Cd_{inorg} in the solutions is thus Cd^{2+} .

^b Cadmium concentrations were originally $\leq 4\%$ of Cd added.

^c DOC = dissolved organic carbon.

solution of the E horizon was so close ($r = 0.977$) that no other transport mechanism than organic matter complexation seems possible.

Recent analytical metal speciation studies (Berggren, 1989) support the conclusions from the statistical treatment of soil solution chemistry. Copper and Pb were mainly present as humic complexes in an acid forest A horizon soil solution, whereas Cd was mainly present as Cd^{2+} (Fig. 6). The DOC (dissolved organic carbon) concentration in the solution was relatively low (9.8 mg l^{-1}) compared with the $100\text{--}150\text{ mg l}^{-1}$ found in soil solutions from the E horizon of a Swedish podzol (Nilsson and Bergkvist, 1983; Bergkvist, 1987b). In such a soil solution an appreciable fraction of even Cd is complexed to humic substances (Table 1).

Besides the DOC concentration, pH also plays an important role in metal-humic substance complexation. The complexation increases with pH. In natural forest soil solutions, Fe and Al compete with trace metals, for example Cu and Pb, for complexing sites on the humic substance molecules. This is another important factor determining the complexation of trace metals by humic substances. The complexation of Al and Fe, however, will also cause polymerization of the molecules (e.g. Ritchie and Posner, 1982), making investigations difficult.

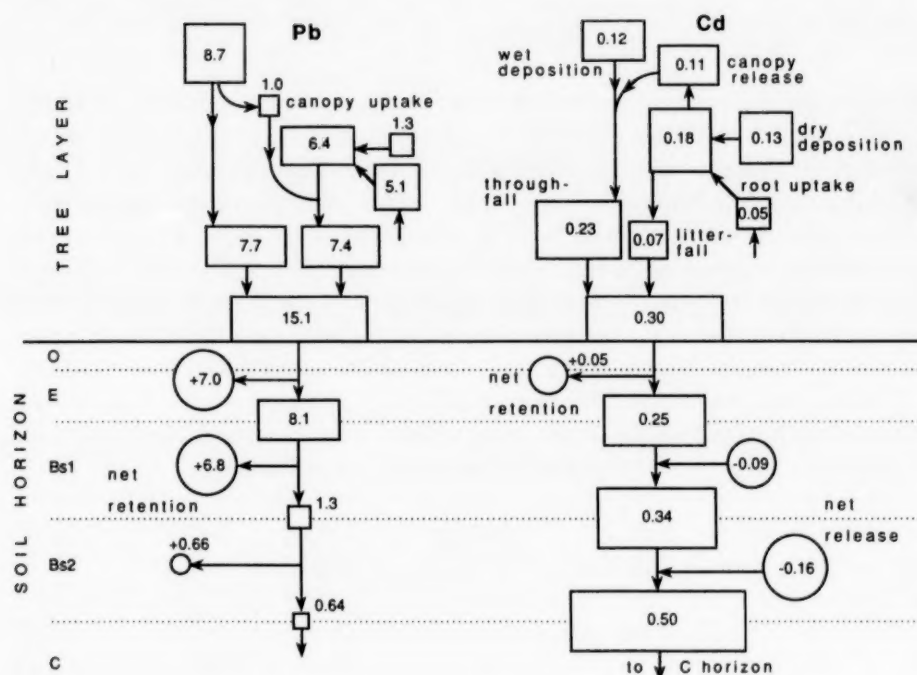


Fig. 7. Deposition and cycling of Pb and Cd in a mature spruce forest (Värsjö) in south Sweden. Compartment size is proportional to the annual flux through plant cover and soil ($\text{mg m}^{-2} \text{year}^{-1}$). Redrawn from Bergkvist (1987b). Dry deposition from Wiman (1984) and Wiman (personal communication).

ECOSYSTEM FLUXES

A mature spruce forest in Scania, where the fluxes of metals were measured for several years, lost $3.1 \text{ g m}^{-2} \text{year}^{-1}$ of Al to the C horizon, whereas only 0.2–0.3 g was supplied as wet + dry deposition (Bergkvist, 1987b). The corresponding figures for Cd were 0.50 and 0.25 mg, respectively (Fig. 7). For Pb and Fe, however, the budgets were strongly positive. Leaching output of Pb was only 0.6 mg compared with a deposition of 10 mg (Fig. 7). For Fe, these figures were 0.04 g and 0.18 g, respectively, in spite of the fact that 1.1 g was released and transported from the O + E horizon with humic matter. There was an almost quantitative reprecipitation of this Fe in the B horizon.

The fluxes of metals and anions through a forest ecosystem are highly dependent on the tree species forming the stand. The fluxes through four triplet stands of Norway spruce (*Picea abies*), European beech (*Fagus sylvatica*) and silver birch (*Betula pendula*) have been quantified in a 3-year study in Scania. Orthic Podzols as well as Dystric Cambisols are represented. Conifers are efficient in capturing acidic aerosols in their canopies and reduce the pH of the incident precipitation considerably, whereas beech and birch were found to raise the pH by up to 2 units while foliated (Bergkvist et al., 1987b). The throughfall of the spruce stands contributed considerable amounts of sulphate to the soil surface, about 2.5 times the amounts in the beech or birch stands (Fig. 8). In all stands, the sulphate budget was positive, input to the soil exceeding output from the B horizons.

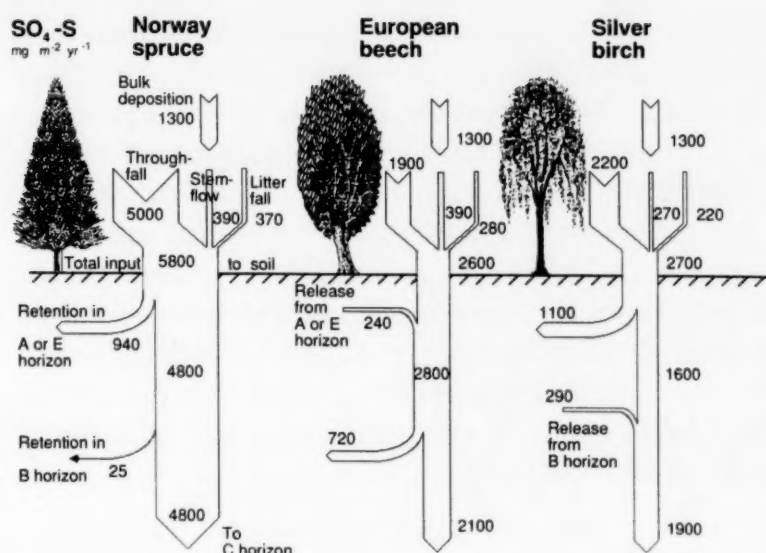


Fig. 8. Annual flux of SO₄-S in compartments of Norway spruce, European beech and Silver birch forest ecosystems adjoining each other in regional deposition baseline areas of Scania, southernmost Sweden. Average of four sites sampled from June 1984 to May 1987. At each of the four sites, bulk deposition was measured using four open funnels. Throughfall was collected in 15 funnels in each stand, soil solution from the E horizon in three 0–15 cm monoliths contained in plexiglass percolation lysimeters and from the B horizon in three 0–50 cm lysimeters. Sulphate analysis by ion chromatography.

In contrast to sulphate, Al had a negligible above-ground flux compared with the flux in the soil (Fig. 9). The output from the B horizons was 22 times the input in the spruce ecosystems, 57 times in the beech and only 5 times in the birch. Spruce and beech soils in south Sweden thus have an enormous capability of leaching Al when acidified. The leaching is apparently much lower under the less acidic conditions prevailing in soils of birch stands close to the spruce and beech stands.

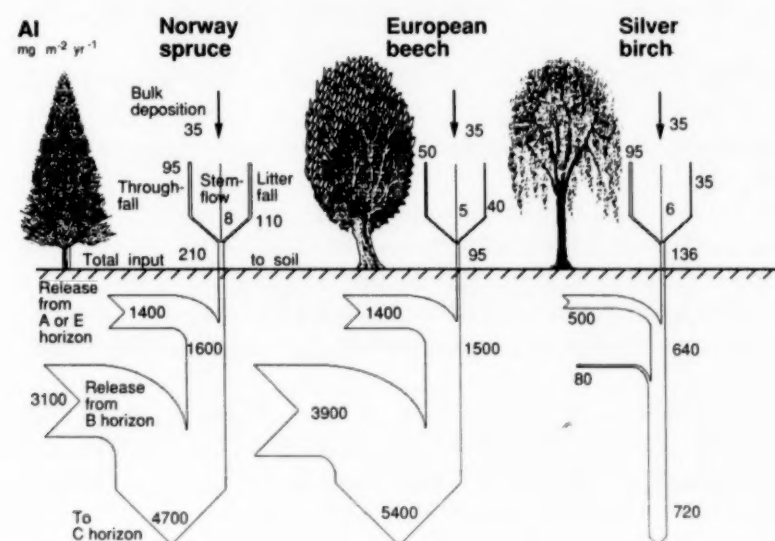


Fig. 9. Annual flux of Al in spruce, beech and birch forest ecosystems, analyzed by atomic absorption spectrophotometry. For further information see Fig. 8.

When the soil profiles down to the C horizons of these adjoining stands of spruce, beech and birch were compared (Bergkvist et al., in preparation), spruce soil proved to be more acid than beech soil throughout the soil profiles. The birch soils always had the highest pH. These differences were partly consistent with differences in throughfall deposition rates between the stands, as shown in Fig. 8. Therefore, spruce seems to exert a more powerful influence than beech on the leaching of metals from the soil, although beech also increased the release of metals considerably. Spruce is known to have a higher internal annual production of acid in combination with a higher deposition rate of acidifying substances in the canopy compared with a deciduous forest or an open area (Nihlgård, 1970; Mayer and Ulrich, 1977; Matzner and Ulrich, 1981; Skeffington, 1983; Bergkvist et al., 1987a,b).

CONCLUSION

In conclusion, forest soils of south Sweden are losing base cations, Al, Cd and Zn due to increased leaching rates following soil acidification. In contrast, budgets are positive for Pb and Fe, elements with a high affinity for humic matter.

REFERENCES

- Åberg, G., G. Jacks and P.J. Hamilton, 1989. Weathering rates and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios: an isotopic approach. *J. Hydrol.*, 109: 65–78.
- Bache, B.W., 1980. The acidification of soils. In: T.C. Hutchinson and M. Havas (Eds), *Effect of Acid Precipitation on Terrestrial Ecosystems*. Plenum Press, New York, p. 183.
- Berdén M., S.I. Nilsson, K. Rosén and G. Tyler, 1987. Soil acidification, extent, causes and consequences. An evaluation of literature information and current research. National Swedish Environment Protection Board, Report 3292, Solna, Sweden, 164 pp.
- Berggren, D., 1989. Speciation of aluminium, cadmium, copper, and lead in humic soil solutions — a comparison of the ion exchange column procedure and equilibrium dialysis. *Int. J. Environ. Anal. Chem.*, 45: 1–15.
- Bergkvist, B., 1987a. Leaching of metals from forest soils as influenced by tree species and management. *For. Ecol. Manage.*, 22: 29–56.
- Bergkvist, B., 1987b. Soil solution chemistry and metal budgets of spruce forest ecosystems in south Sweden. *Water, Air Soil Pollut.*, 33: 131–154.
- Bergkvist, B., L. Folkeson and K. Olsson, 1987a. Fluxes of protons, metals and anions in spruce, beech and birch forest ecosystems. In: *Direct Effects of Dry and Wet Deposition on Forest Ecosystems — In Particular Canopy Interactions*. Proc. Workshop, Lökeberg, Sweden, 19–23 October 1986. Commission of the European Communities, Directorate-General for Science, Research and Development, Environment Research Programme. EUR 11264. Air Pollution Research Report 4, pp. 79–85.
- Bergkvist, B., L. Folkeson and K. Olsson, 1987b. Metal fluxes in *Picea abies*, *Fagus sylvatica* and *Betula pendula* forest ecosystems. In: S.E. Lindberg and T.C. Hutchinson (Eds), *Int. Conf. Heavy Metals in the Environment*, New Orleans, Sept. 1987. CEP Consultants Ltd, Edinburgh, Vol. 2, pp. 407–409.
- Cronan, C.S., J.N. Kelly, C.L. Schofield and R.A. Goldstein, 1987. Aluminium geochemistry and tree toxicity in forests exposed to acidic deposition. In: *Acid Rain: Scientific and Technical Advances*. Selper, London, pp. 649–656.

- Dahl, E., 1988. Acidification of Soils in the Rondane Mountains, South Norway, due to acid precipitation. *Økoforsk*, 1: 1-53. Ås, Norway.
- Driscoll, C.T., 1984. A procedure for the fractionation of aqueous aluminium in dilute acid waters. *Int. J. Environ. Anal. Chem.*, 16: 267-283.
- Falkengren-Grerup, U., 1987. Long-term changes in pH of forest soils in southern Sweden. *Environ. Pollut.*, 43: 79-90.
- Falkengren-Grerup, U., N. Linnermark and G. Tyler, 1987. Changes in acidity and cation pools of south Swedish soils between 1949 and 1985. *Chemosphere*, 16: 2239-2248.
- Fölster, H., 1985. Proton consumption rates in Holocene and present-day weathering of acid forest soils. In: J.I. Drever (Ed.), *The Chemistry of Weathering*. Reidel, Dordrecht, The Netherlands, pp. 197-209.
- Hallbäcken, L. and C.O. Tamm, 1986. Changes in soil acidity from 1927 to 1982-1984 in a forest area of southwest Sweden. *Scand. J. For. Res.*, 1: 219-232.
- Helgeson, H.C., W.M. Murphy and P. Aagaard, 1984. Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions II. Rate constants, effective surface area and the hydrolysis of feldspar. *Geochim. Cosmochim. Acta*, 48: 2405-2432.
- Jacks, G., S. Andersson and B. Stegman, 1989. pH-changes over 30-40 years along a deposition gradient. In: I. Szabolcs (Ed.), *Proc. Conf. Environmental Threats to Forest and Other Ecosystems*, Oulu, Finland. The Academy of Finland.
- LaZerte, B.D., 1984. Forms of aqueous aluminium in acidified catchments of central Ontario: a methodological analysis. *Can. J. Fish. Aquat. Sci.*, 41: 766-776.
- Lindsay, W.L., 1979. *Chemical Equilibria in Soils*. Wiley, New York, 449 pp.
- Matzner, E. and B. Ulrich, 1981. Bilanzierung jährlicher Elementflüsse in Waldökosystemen im Solling. *Z. Pflanzenernaehr. Bodenk.*, 144: 660-681.
- Mayer, R. and B. Ulrich, 1977. Acidity of precipitation as influenced by the filtering of atmospheric sulphur and nitrogen compounds. Its role in the element balance and effect on soil. *Water, Air Soil Pollut.*, 7: 409-416.
- Nihlgård, B., 1970. Precipitation, its chemical composition and effect on soil water in a beech and a spruce forest in south Sweden. *Oikos*, 21: 208-217.
- Nilsson, S.I. and B. Bergkvist, 1983. Aluminium chemistry and acidification processes in a shallow podzol on the Swedish westcoast. *Water, Air Soil Pollut.*, 20: 311-329.
- Olsson, M. and P-A. Melkerud, 1989. Chemical and mineralogical changes during genesis of a podzol from sandy till in southern Sweden. *Geoderma*, 45: 267-287.
- Risinger, L., G. Johansson and T. Thorneman, 1989. Optimization of flow-through cells for dialysis and other membrane separations in flow injection analysis using a laminar flow model. *Anal. Chim. Acta*, 224: 13-22.
- Ritchie, G.S.P. and A.M. Posner, 1982. The effect of pH and metal binding on the transport properties of humic acids. *J. Soil Sci.*, 33: 233-247.
- Seip, H.M., L. Müller and A. Naas, 1984. Aluminium speciation: Comparison of two spectrophotometric analytical methods and observed concentrations in some acid aquatic systems in southern Norway. *Water, Air Soil Pollut.*, 23: 81-95.
- Skeffington, R.A., 1983. Soil properties under three species of tree in southern England in relation to acid deposition in throughfall. In: B. Ulrich and J. Pankrath (Eds), *Effects of Accumulation of Air Pollutants in Forest Ecosystems*. D. Reidel Publishing Company, Dordrecht, pp. 219-231.
- Tamm, C.O. and L. Hallbäcken, 1988. Changes in soil acidity in two forest areas with different acid deposition: 1920s to 1980s. *Ambio*, 17: 56-61.
- Tyler, G., 1981. Leaching of metals from the A-horizon of a spruce forest soil. *Water, Air Soil Pollut.*, 15: 353-369.
- Tyler, G., D. Berggren, B. Bergkvist, U. Falkengren-Grerup, L. Folkesson and Å. Rühling, 1987. Soil acidification and metal solubility in forests of southern Sweden. In: T.C. Hutchinson and K.M. Meema (Eds), *Effects of Atmospheric Pollutants on Forests, Wetlands and Agricultural Ecosystems*. NATO ASI Series, Vol. G16, Springer-Verlag, Berlin, Heidelberg, pp. 347-359.
- Ulrich, B., 1983. Soil acidity and its relations to acid deposition. In: B. Ulrich and J. Pankrath (Eds), *Effects of Accumulation of Air pollutants in Forest Ecosystems*. D. Reidel Publishing

Company, Dordrecht, pp. 127-146.

Wiman, B., 1984. Aerosol dry deposition of heavy metals and acids to forest ecosystems. National Swedish Environmental Protection Board, PM 1908, Solna, Sweden, 63 pp.

Yang, X., L. Risinger and G. Johansson, 1987. Removal of humic acid and surfactant interferences in trace metal determination by differential-pulse and PC stripping voltammetry with use of adsorption and chelate ion-exchanger columns in a flow-injection system. *Anal. Chim. Acta*, 192: 1-8.

OCCURRENCE OF HEAVY METALS IN WATER, PHYTOPLANKTON AND ZOOPLANKTON OF A MESOTROPHIC LAKE IN EASTERN POLAND

S. RADWAN, W. KOWALIK and C. KOWALCZYK

Department of Zoology and Hydrobiology, Agricultural Academy, Akademicka 13, 20-934 Lublin (Poland)

ABSTRACT

The concentrations of the heavy metals Cu, Zn, Mn, Fe, Cd, Pb and Co have been determined in phytoplankton, zooplankton and water of the mesotrophic Lake Piaseczno (eastern Poland). The zooplankton community consists of three basic groups, *Rotaria*, *Cladocera* and *Copepoda*, which were caught in light traps. Net phytoplankton is represented mainly by *Chlorophyta* and *Conjugatea*. The concentrations of heavy metals differed in phytoplankton and zooplankton, especially with respect to Mn, Pb, Cu and Cd. Some preference in absorption of microelements by phytoplankton and zooplankton has been found.

INTRODUCTION

Numerous papers have been published which deal with the occurrence of heavy metals in the various components of aqueous ecosystems (Baccini and Sauter, 1979; Förstner and Wittman, 1979; Bubicz et al., 1982; Moore and Ramamoorthy, 1984). However, only a few papers refer to the presence of heavy metals in zooplankton and phytoplankton in fresh water. A large number of papers has discussed the problem of sorption of heavy metals by algal species either under laboratory conditions or in situ (Lorch et al., 1977; Wong et al., 1978; Hart et al., 1979; Cain et al., 1980; Skowroński, 1984), but few papers have dealt either with the content of microelements separately in phytoplankton and zooplankton species in the natural environment or with correlations between concentrations of these elements in plankton and water (e.g. Kerrison et al., 1988; Radwan et al., 1989). Determination of these metals in zooplankton and phytoplankton is not easy due to the difficulties in separating these two plankton communities under natural conditions (Förstner and Wittman, 1979).

Bearing in mind the scarce information on the occurrence of heavy metals in zooplankton and phytoplankton, the two most important communities in still water ecosystems, an attempt is made to determine the concentration of heavy metals in plankton and correlate the results with concentrations in water.

SITE DESCRIPTION, MATERIALS AND METHODS

The studies were carried out in the mesotrophic Lake Piaseczno situated in the Łeczna-Włodawa Lake District (E. Poland). The lake has no outlet and covers an area of 85 ha. The maximum depth is 38.8 m. Its thermal-oxygen conditions change during the year, typical of holomictic lakes. Average values for basic physico-chemical factors are: visibility (Secchi disc), 6.2 m; pH, 7.3; COD, 11.26 mg O₂ l⁻¹; BOD, 1.71 mg O₂ l⁻¹; and temperature ranging from 9°C in spring to 24°C in summer.

The average concentrations of ammonium, nitrate, phosphate, calcium and magnesium ions are, respectively, 0.008, 0.17, 0.012, 6.18, and 1.63 mg l⁻¹.

In the summer of 1988, the concentrations of Cu, Zn, Mn, Fe, Cd, Pb and Co were determined in zooplankton, phytoplankton and water from Lake Piaseczno.

For "clean" sampling of zooplankton, light traps of the Kowalczyk and Kowalik (1979) type were used. These traps, due to positive phototactic behavior by zooplankton, enabled large amounts of zooplankton to be obtained during night sampling. Simultaneously, net plankton (phyto- and zooplankton) was sampled using a net with 55 µm mesh size. The concentrations of heavy metals in the "clean" zooplankton and net plankton samples were determined by atomic absorption spectrophotometry (AAS). The concentration of a given metal in the phytoplankton was calculated on the basis of the difference in the values for that metal in net plankton (phyto- and zooplankton) and in "clean" zooplankton.

Bioaccumulation indices were calculated for phyto- and zooplankton; this indicator expresses the ratio of metal concentration in a plankton community to its concentration in water.

RESULTS AND DISCUSSION

Water

The average concentration of heavy metals both in the surface and bottom layers of Lake Piaseczno was at a low and immutable level. Four of the studied trace metals exhibited high average concentrations, with the following order of abundance (µg l⁻¹): Fe (60), Zn (58), Mn (32) and Pb (18). The remaining three trace metals exhibited lower average concentrations: Cu (15), Co (3) and Cd (1). The metals occurred in a slightly different order in the rivers of the region, where one group of microelements consisted of Zn > Pb > Fe > Cu and a second group of Co > Cd > Mn (Bubicz et al., 1982).

In natural and relatively clean surface waters in the other regions of Poland, the heavy metals content is similar and probably depends upon background geochemistry and human activity (Wieclawski, 1972; Starmach et al., 1978; Reczyńska-Dutka, 1982, 1985).

TABLE 1

Average^a heavy metal concentrations in the water and plankton of Lake Piaseczno in 1988 (summer)

		Cu	Zn	Fe	Mn	Cd	Pb	Co
Water	($\mu\text{g l}^{-1}$)	15.0	58.2	60.0	32.5	1.1	18.0	3.0
Net phytoplankton	($\mu\text{g g}^{-1}$ wet wt)	11.3	822.5	2202.5	1286.1	0.2	6.5	0.3
Zooplankton	($\mu\text{g g}^{-1}$ wet wt)	36.9	926.0	2185.0	177.7	1.1	9.3	0.2

^aAverage of three determinations.

Plankton (phyto- and zooplankton)

In Lake Piaseczno, net phytoplankton was represented mainly by *Chlorophyta* and *Conjugatae*. Among the *Chlorophyta* the dominant species were those from the genus *Zygnema*. Three basic groups, *Rotatoria*, *Cladocera* and *Copepoda*, constituted the zooplankton. In this ecological community the dominating species were *Kellicottia longispina* (Kell.), *Polyarthra vulgaris*

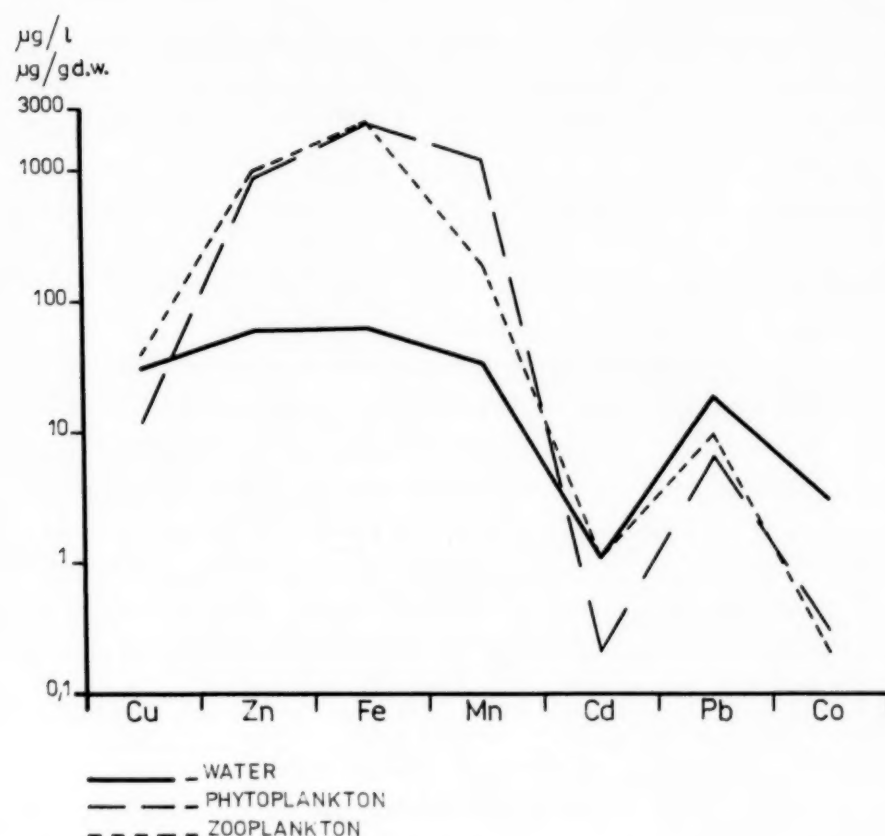


Fig. 1. Concentrations of heavy metals in water, phytoplankton and zooplankton of Lake Piaseczno.

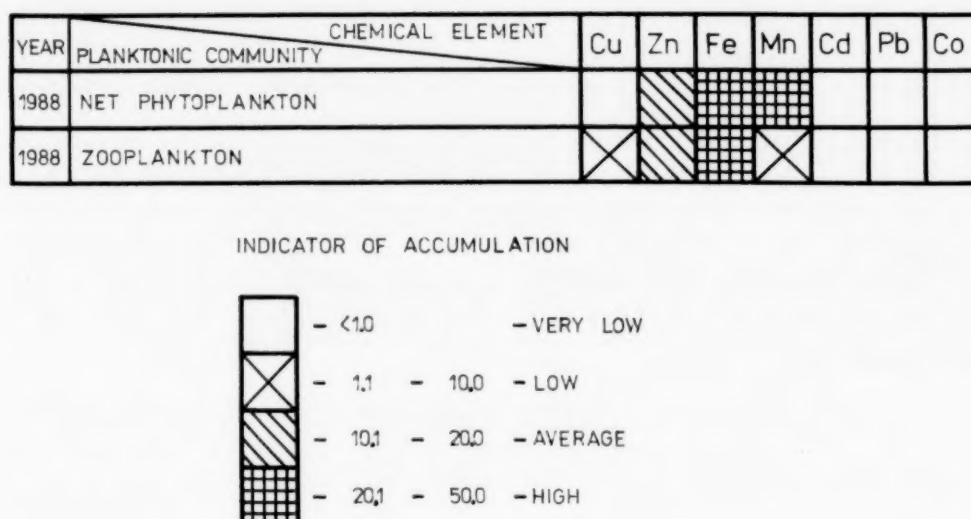


Fig. 2. Bioaccumulation indices of heavy metals by phytoplankton and zooplankton in Lake Piaseczno.

Carl. and *Conochilus unicornis* Rouss. (*Rotatoria*), *Bosmina coregoni kessleri* Ulj. and *Ceriodaphnia quadrangula* Müll. (*Cladocera*), and *Mesocyclops leuckarti* Claus (*Copepoda*).

There was a difference between the two plankton communities with respect to heavy metal concentrations. In the summer, net phytoplankton contained high average values of Fe, Mn and Zn (Table 1, Fig. 1). The bioaccumulation indices for these trace metals were: Fe, 36.7; Mn, 40.1; and Zn, 14. The average value for Cu was considerably lower at $11.3 \mu\text{g g}^{-1}$ dry matter with an accumulation index of 0.4. Lead, Cd and Co occurred in much lower concentrations in the net phytoplankton, ranging from 0.2 to $6.5 \mu\text{g g}^{-1}$ dry matter (Table 1). The accumulation indices for these metals were < 1.0 (Fig. 2).

In the summer, zooplankton exhibited high concentrations of Fe and Zn, with average values of 2185 and $926 \mu\text{g g}^{-1}$ dry matter, respectively. Their bioaccumulation indices were also high at 36.4 and 16.0, respectively. Manganese and Cu in this community were at considerably lower concentrations than those of Fe and Zn: 177.7 and $36.9 \mu\text{g g}^{-1}$ dry matter and bioaccumulation indices of 5.4 and 2.4, respectively. Three other trace elements (Pb > Cd > Co) formed a group with low concentrations and low bioaccumulation indices. The concentrations of these metals in zooplankton were ($\mu\text{g g}^{-1}$ dry matter): 9.3, 1.1 and 0.2, with bioaccumulation indices of 0.5, 1.0 and 0.06, respectively (Table 1, Figs 1 and 2).

In both plankton communities, the examined trace metals formed two groups. The first group, with high bioaccumulation indices, consists of Fe > Mn > Zn, and the second group, with very low bioaccumulation indices, consists of Pb > Cd > Co. Only Cu was present at similar concentrations in all three components of the lake ecosystem (water, phyto- and zooplankton) (Table 1, Figs 1 and 2).

There was, however, a clear difference in average concentrations of some

heavy metals in the two plankton communities. The Mn concentration in the net phytoplankton was seven times that in the zooplankton. A high concentration of Mn in phytoplankton has also been confirmed by other authors (Starmach et al., 1978). Lead, Cu and Cd, however, were present at from 1.4 to 4 times higher values in the zooplankton than in the phytoplankton. The average levels of Fe, Zn and Co were similar in both plankton communities (Table 1, Fig. 1).

High bioaccumulation indices for Fe, Mn and Zn in both plankton communities may indicate rapid uptake of these trace metals by small planktonic organisms. Copper was taken up more slowly than the other three trace metals (especially by phytoplankton), and Co, Pb and Cd, characterized by low or very low bioaccumulation indices, were the slowest to be absorbed by the plankton (Fig. 2). Similar results for bioaccumulation of Cd and Cu by plankton were observed during an experiment carried out in Lake Comabbio, Italy (Kerrison et al., 1988). The rate of bioaccumulation depends on many factors, such as water fertility and chemical composition, qualitative and quantitative plankton species composition and season. Bioaccumulation is most active in summer, when small algae dominate lake phytoplankton, and rotifers and cladocerans dominate lake zooplankton. The above-mentioned groups of zooplankton and phytoplankton are the most sensitive absorbents of microelements (Marshall and Mellinger, 1980; Kerrison et al., 1988).

The studies in Lake Piaseczno were carried out in the summer and the bioaccumulation of seven trace metals in the phytoplankton and zooplankton observed under natural conditions seems to confirm the results obtained by other authors for heavy metals (Cd, Cu) in laboratory and field experiments (Kerrison et al., 1988).

CONCLUSIONS

(i) For both communities (phytoplankton and zooplankton) the highest metal concentrations were exhibited by iron, zinc and manganese. These levels were many times higher than the levels in water (Table 1, Fig. 1).

(ii) Manganese was at a higher concentration in the phytoplankton than in the zooplankton, and lead, copper and cadmium were at higher concentrations in the zooplankton than in the phytoplankton.

(iii) High bioaccumulation indices for both plankton communities were found for iron, manganese and zinc, and very low indices were found for lead and cadmium. This may be evidence of the rate and selective uptake of particular trace metals by the phytoplankton and zooplankton. If the bioaccumulation index for one trace metal is higher than that of a second trace metal, then the former is absorbed more rapidly from water by a given plankton community.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the support received from CPBP (No. 04.10.16).

REFERENCES

- Baccini, P. and A. Sauter, 1979. MELIMEX. An experimental heavy metal pollution study: chemical speciation and biological availability of copper in lake water. *Schweiz. Z. Hydrol.*, 41: 291-314.
- Bubicz, M. L. Kozak, M. Mikos and Z. Warda, 1982. Heavy metals in the aquatic environment of some water bodies of the Lublin coal basin. *Acta Hydrobiol.*, 24: 125-138.
- Cain, I.R., D.C. Paschal and C.M. Hayden, 1980. Toxicity and bioaccumulation of cadmium in the colonial green algae, *Scenedesmus obliquus* Arch. Environ. Contam. Toxicol., 9: 9-16.
- Förstner, U. and G.T.W. Wittman, 1979. Metal Pollution in the Aquatic Environment. Springer-Verlag, Berlin, p. 486.
- Hart, B.A., P.E. Bertram and B.D. Scaife, 1979. Cadmium transport by *Chlorella pyrenoidosa*. *Environ. Res.*, 18: 327-335.
- Kerrison, P.H., A.R. Sprocati, O. Ravera and L. Amantini, 1988. Effects of cadmium on an aquatic community using artificial enclosures. *Environ. Technol. Lett.*, 3: 169-175.
- Kowalczyk, C. and W. Kowalik, 1979. A new model of a plankton light trap. *Wiad. Ekol.*, 16: 68-76.
- Lorch, D.W., M. Melkonian, A. Weber and M. Wettren, 1977. Reasons for different lead accumulation by green algae. Some experiments—some suggestions. *Abstr. SIL XX Congr.*, Copenhagen, pp. 172-173.
- Marshall, J.S. and P.L. Mellinger, 1980. An in situ experimental method for toxicological studies on natural plankton-communities. In: J.G. Eaton, P.R. Parrish and A.C. Hendricks (Eds), *Aquatic Toxicology*, ASTM STP 707. Am. Soc. for Testing and Materials, Philadelphia, PA, pp. 27-39.
- Moore, J.W. and S. Ramamoorthy, 1984. Heavy Metals in Natural Waters—Applied Monitoring and Impact Assessment. Springer Verlag, New York.
- Radwan, S., W. Kowalik and C. Kowalczyk, 1989. Occurrence of heavy metals in the waters, bottom sediments and macrophytes in the Piaseczno Lake. In: *Ochrona zdrowia i środowiska człowieka w warunkach uprzemysłowienia*. Wyd. Polon., Lublin (in press).
- Reczyńska-Dutka, M., 1982. Stream ecosystems in mountain grassland (West Carpathians). Heavy metals. *Acta Hydrobiol.*, 24: 337-341.
- Reczyńska-Dutka, M., 1985. Ecology of some waters in the forest-agricultural basin of the River Brynica near the Upper Silesian Industrial Region. 3. Chemical composition of the water. Heavy metals. *Acta Hydrobiol.*, 27: 451-464.
- Skowroński, T. 1984. Uptake of cadmium by *Stichococcus bacillaris*. *Chemosphere*, 13: 1385-1389.
- Starmach, K. S. Wróbel and K. Pasternak, 1978. *Hydrobiologia*. PWN, Warszawa, p. 631.
- Wieclawski, F., 1972. Investigations on the changes in the content of heavy metals in lake waters of the Masurian Lake District. *Acta Hydrobiol.*, 14: 149-163.
- Wong, P.T.S., Y.K. Chan and P.L. Luxon, 1978. Toxicity of a mixture of metals on freshwater algae. *J. Fish. Res. Board Can.*, 35: 479-481.

ACCUMULATION OF HEAVY METALS IN A LAKE ECOSYSTEM

S. RADWAN, W. KOWALIK and R. KORNIJÓW

*Department of Zoology and Hydrobiology, Agricultural Academy, ul. Akademicka 13, 20-394
Lublin (Poland)*

ABSTRACT

The concentrations of Cu, Zn, Fe, Mn, Ni, Cd, Pb and Co have been determined in water, bottom sediments, plankton, zoobenthos and ichthyofauna of mesotrophic Lake Piaseczno located in eastern Poland. In water, sediments, plankton and benthos the most abundant heavy metals were Fe, Zn and Mn, whereas in fish Zn, Cu and Mn were most abundant. The amount of heavy metals in the biotic components was dependent upon their concentration in water and partly upon the concentration in bottom sediments. A considerably less important role in the translocation of heavy metals is probably played by trophic interactions.

INTRODUCTION

Concentrations of heavy metals in water and bottom sediments have been studied by numerous authors (Baccini and Sauter, 1979; Bubicz et al., 1982; Moore and Ramamoorthy, 1984). However, in Poland few papers have been published dealing with the occurrence of heavy metals in different fish species, and little emphasis has been placed upon heavy metal concentrations in fish internal organs (Juszkiewicz and Szkoda, 1985; Mikos et al., 1986). Little information also exists concerning the concentrations of heavy metals in invertebrates and almost no research has been carried out on the concentrations of these metals in the basic trophic elements of a lake ecosystem (Wachs, 1985; Kerrison et al., 1988).

In order to investigate the translocation of heavy metals in a lake ecosystem, studies have been carried out on their accumulation in the basic trophic elements, that is in water, bottom sediments, plankton, zoobenthos and fish.

MATERIALS AND METHODS

Samples were collected from the small mesotrophic Lake Piaseczno situated in the Łęczna-Włodawa lakeland area, eastern Poland. Sampling took place during the summers of 1987 and 1988. The concentrations of Zn, Mn, Fe, Cu, Cd, Ni and Co in water, bottom sediments, plankton (phyto- and zooplankton), macrozoobenthos and some species of fish (both predatory and non-predatory) were analyzed by means of atomic absorption spectrometry.

Water was sampled near the surface and from bottom layers of the lake at

depths of 0.5 and 25 m, respectively. Whatman GF/C filters were used to filter water samples, and concentrations of Zn, Mn, Fe and Cu were determined in methylisobutylketone extracts.

Bottom sediments were collected from both the shallow littoral (0.5 m) and profundal zones (25 m) using Kajak-type tubular apparatus (Kajak et al., 1965). The samples were dried at 105°C, ground and mineralized in a mixture of $\text{HNO}_3 + \text{HClO}_4$ acids (7:1). Following mineralization, Cu, Mn, Zn and Fe were determined in the solution and Co, Cd and Pb in the extract.

Zoobenthos were sampled with Kajak-type tubular apparatus. Before analysis, the animals were starved for > 24 h to empty their alimentary canals. Plankton was collected vertically using a plankton net of 0.05 mm diameter net mesh. Determination of heavy metals in plankton, zoobenthos and fish (*Abramis brama*, *Tinca tinca*, *Esox lucius*, and *Perca fluviatilis*) was carried out as for bottom sediments (see above). The results are expressed as mean values in micrograms per litre water or as micrograms per gram dry matter. Five replicates of each sample were analyzed. In addition, the indices of heavy metal accumulation in the lake ecosystem were assessed and expressed as the ratio of mean microelement concentration in each ecosystem element divided by its mean concentration in filtered water.

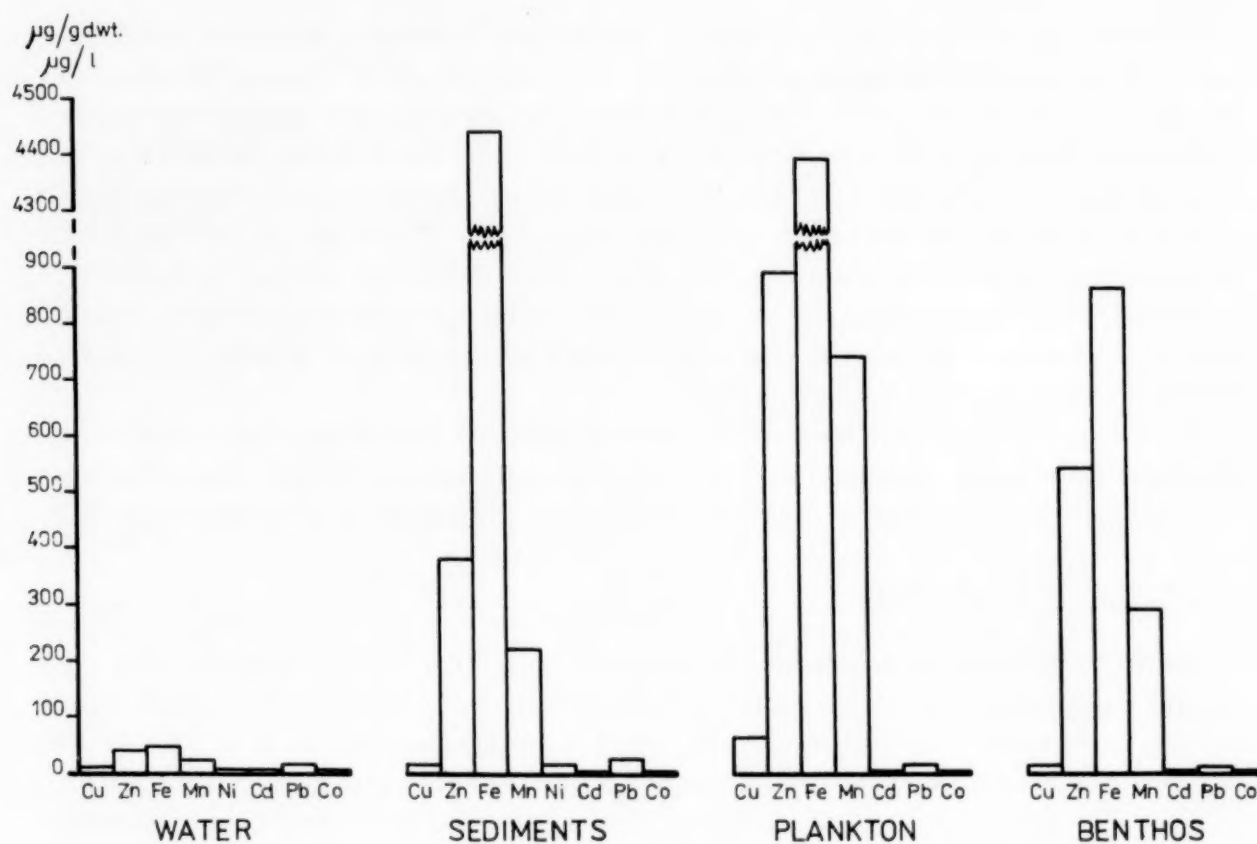


Fig. 1. Average concentrations of heavy metals in selected elements of Lake Piaseczno.

OCCURRENCE OF HEAVY METALS IN ABIOTIC COMPONENTS

Water

The average heavy metal content of the surface and bottom layers of water from Lake Piaseczno was relatively low, varying from $2.8 \mu\text{g l}^{-1}$ for Co to $43.5 \mu\text{g l}^{-1}$ for Fe (Fig. 1). The values decreased in the order $\text{Fe} > \text{Zn} > \text{Mn} > \text{Ni} > \text{Pb} > \text{Cu} > \text{Cd} > \text{Co}$. The concentrations of most of the metals in the lake water were similar to those reported for other Polish lakes and rivers (Bubicz et al., 1982; Reczyńska-Dutka, 1985). Only two microelements, Cu and Mn, reached a higher level in Lake Piaseczno than in river waters from this region (Radwan et al., 1989).

Bottom sediments

Sandy gyttja was the main component of the bottom sediments from Lake Piaseczno and contained from 21 to 45% organic matter.

The heavy metal concentrations in the bottom sediment from Lake Piaseczno varied widely (Fig. 1). Iron was the most abundant with an average

CHEMICAL ELEMENT BIOCOENOSES ELEMENT	Cu	Zn	Fe	Mn	Ni	Cd	Pb	Co
SEDIMENTS	X	X	X	X	X	X	X	X
PLANKTON	X	X	X	X	—	X	X	X
ZOOBENTHOS	X	X	X	X	—	X	X	X
ABRAMIS BRAMA	X	X	X	X	X	X	X	—
TINCA TINCA	X	X	—	X	X	X	X	—
ESOX LUCIUS	X	X	—	X	X	X	X	—
PERCA FLUVIATILIS	X	X	X	X	X	X	X	—

COEFFICIENT OF THE ACCUMULATION

	—	<1,0	—	VERY LOW
	—	1,1 — 10,0	—	LOW
	—	10,1 — 20,0	—	AVERAGE
	—	20,1 — 50,0	—	HIGH
	—	>50,0	—	VERY HIGH
—	—	NOT ANALYSED		

Fig. 2. Accumulation coefficients of heavy metals in selected elements of Lake Piaseczno.

concentration of $4439.4 \mu\text{g g}^{-1}$ dry matter. Zinc and manganese concentrations were fairly high (381.8 and $249.1 \mu\text{g g}^{-1}$ dry matter, respectively). The remaining metals occurred in much smaller amounts, ranging from 0.2 to $23.7 \mu\text{g g}^{-1}$ dry matter. Some of the microelements, such as Zn, Pb and Cu, were enriched in the sediments, which contained high levels of detritus. A correlation between heavy metal concentrations and organic matter has also been observed by other authors (Wachs, 1985; Mikos et al., 1986). The concentrations of Fe, Zn, Mn and Pb in the bottom sediments of Lake Piaseczno were similar or slightly higher than those in other poorly degraded water bodies (Syers et al., 1973; Förstner and Müller, 1974; Walters et al., 1974; Bubicz et al., 1982; Frye and Shrimp, 1983). Only Cu and Co were generally at lower concentrations than reported for other water bodies.

The average concentrations for most of the heavy metals in bottom sediments were much higher than those in water. Similar findings have been reported by other authors (Burrows and Whitton, 1983; Mikos et al., 1986). Only Cd and Co occurred in higher concentrations in water, which may indicate a considerably slower accumulation of these elements in sediments. Kerrison et al. (1988) also found that Cd accumulated slowly in sediment. They suggested that Cd is probably transferred to sediment by adsorption and settlement.

Accumulation coefficients (Fig. 2) reflect the rate of heavy metal accumulation in sediments. The highest values were found for Fe (150), and the lowest for Cd and Co (0.3 and 0.2, respectively).

ACCUMULATION OF HEAVY METALS IN SOME BIOTIC COMPONENTS

Net plankton

Chlorophyceae and *Conjugatae* were the main phytoplankton taxa, while *Rotifera*, *Cladocera* and *Copepoda* comprised the zooplankton. Species from the genus *Spirogyra* and *Zygnema* predominated among the phytoplankton. The predominate zooplankton species were *Conochilus unicornia*, *Kellicottia longispina*, *Polyarthra vulgaris*, *Bosmina coregoni kessleri*, *Ceriodaphnia quadrangula* and *Mesocyclops leukarti*. There were only a few dead individuals among phyto- and zooplankton.

The concentrations of heavy metals in the net plankton varied from $0.5 \mu\text{g g}^{-1}$ dry matter for Co to $4367.5 \mu\text{g g}^{-1}$ for Fe. The average values for individual metals fell into three groups. Group one is represented by Fe, Zn and Mn. Their average values were high, ranging from 743.2 to $4367.5 \mu\text{g g}^{-1}$ dry matter. A similar concentration pattern has been observed in the case of crustacean plankton in Lake Balaton (Balogh and Salanki, 1984). High concentrations of Zn have also been noted in phytoplankton of Monterey Bay (Knauer and Martin, 1973). The second group consists of the two microelements, Cu and Pb. Their average values ranged from 63.3 to $15.5 \mu\text{g g}^{-1}$ dry matter. These values are similar to those found in Monterey Bay phytoplankton (Knauer and Martin, 1973). The third group also consists of two metals, Ce

and Co, and their average values were low, ranging from 0.5 to 1.1 $\mu\text{g g}^{-1}$ dry matter (Fig. 1). Low Cd concentrations have also been observed in the summer plankton from Lake Comabbio, Italy (Kerrison et al., 1988).

Almost all of the heavy metals occurred in much higher concentrations in net plankton (seston) than in water (Fig. 1). This was particularly evident for Fe, Zn and Mn. Their concentrations in plankton were 25–100 times higher than those in water.

Bioaccumulation coefficients for individual metals in plankton varied considerably. These coefficients were highest for Fe, Zn and Mn, average for Cu, and low or very low for Pb, Cd and Co (Fig. 2). These bioaccumulation coefficients may indicate variations in the selective sorption of heavy metals by plankton. This community is very quick to accumulate Fe, Mn and Zn from water, Cu is accumulated slightly slower, and Pb, Cd and Co very slowly (Radwan et al., 1989). Similar bioaccumulation of Cu and Cd by phytoplankton has been observed in Lake Comabbio in Italy (Kerrison et al., 1988).

Zoobenthos

In the bottom fauna, the most abundant taxa were *Oligochaeta* and *Chironomidae*. Among the *Chironomidae*, the larvae of *Stictochironomus* gr. *psammophilus* and *Procladius skuse* predominated, and among the *Oligochaeta*, *Tubifex tubifex* predominated.

The concentrations of heavy metals in benthic organisms varied widely with large differences between metals. The metals analyzed can be divided into three groups. The first group consists of Fe, Zn and Mn, with concentrations of 858.0, 544.0 and 287.4 $\mu\text{g g}^{-1}$ dry matter, respectively. The second group consists of Cu and Pb, with concentrations of 13.6 and 5.7 $\mu\text{g g}^{-1}$ dry matter, respectively. The last group consists of Cd and Co, with a concentration of 0.4 $\mu\text{g g}^{-1}$ dry matter (Fig. 1).

The concentrations of most of the heavy metals in the bottom fauna corresponded to concentrations in benthos from non-polluted rivers (Leland and McNurney, 1974; Prosi, 1977). However, similar Zn concentrations and considerably higher concentrations of Cd and Cu have been observed in the bottom fauna of highly polluted rivers (Prosi, 1977; Wachs, 1983; Yasuno et al., 1985).

Accumulation coefficients for heavy metals (Fig. 2) followed a similar sequence as their concentrations in the bottom fauna. The highest values were obtained for Zn (50.2), Fe (26.6) and Mn (23.2). A second group with lower coefficients consisted of Cu and Pb (1.0 and 0.8), and a third, consisting of Co and Cd, had very low accumulation coefficients (0.5 and 0.02, respectively). Considerably higher values for this coefficient have been reported by Wachs (1985) for river benthos.

Fish

Heavy metal concentrations were determined in the bone, muscle and liver

TABLE 1

Average concentrations of trace metals ($\mu\text{g g}^{-1}$ dry matter) in selected organs of four fish species from Lake Piaseczno

Species of fish	Cu	Mn	Fe	Zn	Ni	Cd	Pb
<i>Abramis brama</i> (bream)							
Skeleton	3.8	88.5	73.0	490.0	1.6	0.2	1.4
Muscle	26.0	0.7	20.0	36.7	0.05	8.5	0.1
Liver	167.0	6.7		320.0	0	28.0	0
Average concentration	45.3	46.3	45.0	274.7	0.9	11.3	0.8
<i>Tinca tinca</i> (tench)							
Skeleton	7.3	30.0		396.7	1.4	0.2	2.0
Muscle	9.0	1.5	18.0	4.9	0.2	0.07	0.4
Liver	16.0	1.1		47.5	0.3	0.5	0.3
Average concentration	10.8	10.8		149.7	0.6	0.3	0.9
<i>Esox lucius</i> (pike)							
Skeleton	7.3	34.0		590.0	1.6	0.2	1.4
Muscle	6.3	1.6	15.0	7.8	0.1	0.7	0.5
Liver	28.5	4.6		98.0	0.2	9.0	0.4
Average concentration	17.7	11.2		198.5	0.6	4.7	0.7
<i>Perca fluviatilis</i> (perch)							
Skeleton	9.5	46.0	22.0	390.0	1.8	2.7	1.6
Muscle	18.5	2.6	30.0	56.0	0.2	10.7	0.2
Liver	90.0	19.0		350.0	0.3	16.0	0
Average concentration	34.1	17.6	27.0	213.0	0.7	10.0	0.5

of non-predatory fish, specifically *Abramis brama* (bream) and *Tinca tinca* (tench) aged 5–6 years, and of predatory fish, *Esox lucius* (pike) and *Perca fluviatilis* (perch) aged 2–4 years. Considerable differences in heavy metal concentrations were found both between species and between various organs of the same species (Table 1).

The highest average concentration was obtained for Zn in the bones of pike and bream (590 and $490 \mu\text{g g}^{-1}$ dry matter, respectively) and in the liver of perch and bream (350 and $320 \mu\text{g g}^{-1}$ dry matter, respectively). Fairly high Zn concentrations were also found in the muscle of perch ($56 \mu\text{g g}^{-1}$ dry matter) and bream ($36.7 \mu\text{g g}^{-1}$ dry matter).

The average Cu concentration in fish muscle ranged from $6.3 \mu\text{g g}^{-1}$ dry matter in pike to $26 \mu\text{g g}^{-1}$ dry matter in bream. However, the Cu concentrations in bream and perch livers were high (167 and $90 \mu\text{g g}^{-1}$ dry matter, respectively). The higher bioaccumulation of Cu in the liver and of Zn in the kidneys of fish agrees with the results of other workers, e.g. Wachs (1982) and Hakanson (1984).

A fairly high average Mn concentration was found in fish bone (from 30.0 to $88.5 \mu\text{g g}^{-1}$ dry matter), while the values in muscle were low, ranging from 0.7 to $2.6 \mu\text{g g}^{-1}$ dry matter.

The highest average concentrations of Cd were found in bream ($11.3 \mu\text{g g}^{-1}$ dry matter) and perch ($10.0 \mu\text{g g}^{-1}$ dry matter) and the lowest in tench ($0.3 \mu\text{g g}^{-1}$ dry matter). This element is accumulated mainly in liver and bone (Table 1).

The average Pb concentration in fish bones ranged from 1.4 to $2.0 \mu\text{g g}^{-1}$ dry matter, but it was very low in liver, ranging from 0.0 to $0.4 \mu\text{g g}^{-1}$ dry matter. These results do not differ greatly from the average values reported for freshwater fish in Poland (Gajewska and Nabrzyski, 1978).

No clear differences have been found in the average heavy metal accumulation between predatory (pike and perch) and non-predatory (bream and tench) fish. The only exception is the very low Cd concentration observed in tench (Table 1).

The average concentrations of heavy metals in fish decreased in the order:

bream, $\text{Zn} > \text{Cu} > \text{Mn} > \text{Cd} > \text{Fe} > \text{Ni} > \text{Pb}$;
 tench, $\text{Zn} > \text{Cu} = \text{Mn} > \text{Pb} = \text{Ni} > \text{Cd}$;
 pike, $\text{Zn} > \text{Cu} > \text{Mn} > \text{Cd} > \text{Pb} > \text{Ni}$;
 perch, $\text{Zn} > \text{Cu} > \text{Fe} > \text{Mn} > \text{Cd} > \text{Ni} > \text{Pb}$.

The average concentrations of some heavy metals, for example Zn, Cu and Cd, were higher than those obtained in other Polish studies on freshwater and sea fish (Gajewska and Nabrzyski, 1978; Juszkiwicz and Szkoda, 1985).

The bioaccumulation coefficient for microelements in fish bone, muscle and liver was highest in the case of Zn (18.0–33.1) and was considerably lower for Cu (2.2–9.1), Mn (0.8–3.6) and Cd (0.1–1.8). The accumulation of the remaining heavy metals (Fe, Ni and Pb) was low (Fig. 2).

DISCUSSION

In general, the heavy metal content of the various ecological compartments of Lake Piaseczno was fairly high, especially when one considers that the lake does not have any large pollution sources and is far from cities and industrial centres. The relatively high concentrations of metals in water and especially in bottom sediments may be related to the very slow water exchange in the lake. The lake turnover period is estimated to be a few hundred years. It is a lake without inflowing streams and is situated on an impermeable marl substrate. Since the concentrations of most of the examined heavy metals in the deep waters surrounding rock deposited during the cretaceous period did not exceed $0.007 \mu\text{g dm}^{-3}$ (unpublished data), one may suspect that the main source of contamination is precipitation and run-off of mineral fertilizers from cultivated fields.

The bioaccumulation of heavy metals in plankton depends on many factors, e.g. productivity and chemical composition of the water, qualitative and quantitative composition of the plankton (phyto- and zooplankton), sorptive ability of individual species, and season. Metal accumulation is highest in summer. At that time, small algal (e.g. *Chlorella vulgaris*) and zooplankton (*Keratella cochlearis* and *Bosmina coregoni*) species predominate. They can accumulate

some metals, even if the aqueous metal concentrations are low (Marshall and Mellinger, 1980; Kerrison et al., 1988). In the present study, this was true for Fe, Zn, Mn and Cu (Fig. 2).

High Zn, Mn and Fe concentrations in the benthos of Lake Piaseczno may be associated with the dominance structure in which *Oligochaeta* plays the most important role. These animals are considered to be exceptionally susceptible to pollution due to their intensive penetration of bottom sediments (Prosi, 1977). The highest concentration of the above-mentioned microelements in the benthic fauna corresponded to their highest concentration in water and bottom sediments. This supports the hypothesis that water and sediments are the main sources of zoobenthos contamination (Burrows and Whitton, 1983; Wachs, 1985). A slightly different ranking for the microelements with respect to the concentration in water and bottom sediments compared with that in invertebrates may result from different accumulation pathways. For instance, larvae of *Chironomidae* may actively regulate the amounts of individual metals (Walker, 1988). Moreover, some animal cells are capable of active absorption of Zn and Fe (Mess and Wichard, after Wachs, 1985), and this is probably the reason why these two elements exhibited high bioaccumulation coefficients in the bottom fauna of Lake Piaseczno.

However, high bioaccumulation of microelements in the plankton and zoobenthos did not, as a rule, correspond to high levels in fish. This supports the statement of Wachs (1982), who maintained that microelements accumulate in fish mainly by surface adsorption and through branchia, while translocation of these metals through the food chain plays a secondary or unimportant role.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the support received from CPBP (No. 04.10.16).

REFERENCES

- Baccini, P. and A. Sauter, 1979. MELIMEX. An experimental heavy metal pollution study: chemical speciation and biological availability of copper in lake water. *Schweiz. Z. Hydrobiol.*, 41: 291-314.
- Balogh, K.V. and J. Salanki, 1984. Utilization of *Crustacea* zooplankton for estimating heavy metal pollution of Lake Balaton. *Gidrobiol. Zh.*, 20: 56-64.
- Bubicz, M., L. Kozak, M. Mikos and Z. Warda, 1982. Heavy metals in the aquatic environment of some water bodies of the Lublin Coal Basin. *Acta Hydrobiol.*, 24: 125-138.
- Burrows, I.G. and B.A. Whitton, 1983. Heavy metals in water, sediments and invertebrates from a metal-contaminated river free of organic pollution. *Hydrobiologia*, 106: 263-273.
- Förstner, U. and G. Müller, 1974. Schwermetallanreicherungen in detitierten Sedimentkernen aus dem Bodensee und aus dem Tegernsee. *Tschermaks Mineral. Petrogr. Mitt.*, 21: 145-163.
- Frye, J.C. and N.F. Shrimp, 1983. Major, minor and trace elements in sediments of late pleistocene Lake Saline compared with those in Lake Michigan sediments. *Environ. Geol. Note*, 60: 1-14.
- Gajewski, R. and M. Nabrzyski, 1978. Occurrence of some trace metals in sea and fresh-water fish. In: *Proc. First Polish Conf. Effect of Trace Metal Pollution on Agriculture*, pp. 135-143.

- Hakanson, L., 1984. Metals in fish and sediments from the River Kolbäckean water system. Swed. Arch. Hydrobiol., 101: 373-400.
- Juszkiewicz, T. and J. Szkoda, 1985. Content of potentially toxic elements in Polish fresh-water fish. In: Proc. Third Polish Conf. Effect of Trace Metal Pollution on Agriculture, pp. 144-148.
- Kajak, Z., K. Kacprzak and R. Polkowski, 1965. Tubular bottom sampler. Ekol. Pol., Ser. B, 11: 159-165.
- Kerrison, P.H., D. Annonsi, S. Zerini, O. Ravera and B. Moss, 1988. Effects of low concentrations of heavy metals on plankton community dynamics in a small, shallow, fertile lake. J. Plankton Res., 10: 779-812.
- Knauer, G.A. and J.H. Martin, 1973. Seasonal variations of cadmium, copper, manganese, lead and zinc in water and phytoplankton in Monterey Bay, California. Limnol. Oceanogr., 18: 597-604.
- Leland, H.V. and J.M. McNurney, 1974. Lead transport in a river ecosystem. In: Proc. Int. Conf. Transport of Persistent Chemicals in an Aquatic Ecosystem. Ottawa, pp. 17-23.
- Marshall, J.S. and P.L. Mellinger, 1980. An in situ experimental method for toxicological studies on natural plankton communities. In: J.G. Eaton, P.R. Parrish and A.C. Hendricks (Eds.) Aquatic Toxicology, ASTM STP 707. Am. Soc. for Testing and Materials, Philadelphia, PA, pp. 27-39.
- Mikos, M., M. Studnicka, M. Bubicz and Z. Warda, 1986. Heavy metals in chosen water ecological systems. In: Proc. Fourth Int. Conf. Bioindicators Deterioration Regionis, Liblice, 2 July 1982, Ceske Budejovice, pp. 130-143.
- Moore, J.W. and S. Ramamoorthy, 1984. Heavy Metals in Natural Waters—Applied Monitoring and Impact Assessment. Springer Verlag, New York.
- Prosi, F., 1977. Schwermetallbelastung in den sedimenten der Elsenz und Auswirkung auf limnische Organismen. Ph.D. Thesis. University of Heidelberg.
- Radwan, S., W. Kowalik and C. Kowalczyk, 1989. Content of heavy metals in water bottom sediments and macrophytes in Lake Piaseczno. In: Ochrona Zdrowia i Srodowiska Czlowieka w Warunkach Uprzemyslowienia. Lublin, Wyd. Polonia, in press.
- Reczyńska-Dutka, M., 1985. Ecology of some waters in the forest-agricultural basin of the River Brynica near the Upper Silesian Industrial Region. 3. Chemical composition of the water. Heavy metals. Acta Hydrobiol., 27: 451-464.
- Syers, J.K., I.K. Iskander and D.R. Keeney, 1973. Distribution and background levels of mercury in sediment cores from selected Wisconsin lakes. Water, Air Soil Pollut., 2: 105-118.
- Wachs, B., 1982. Schwermetallgehalt von Fischen aus der Donau. Z. Wasser Abwasser Forsch., 15: 43-49.
- Wachs, B., 1983. Bioindikatoren für erhöhte Metallgehalte in Fließgewässern. Naturwissenschaften, 70: 577-580.
- Wachs, B., 1985. Schwermetallgehalt der Benthonorganismen der schiffbaren Mains, 25 Arbeitssagung der Internationalen Arbeitsgemeinschaft Donauforschung, Bratislava, pp. 82-86.
- Walker, P., 1988. The fate of trace metals during metamorphosis in Chironomids. University of Amsterdam, 18 pp.
- Walters, L.J., T.J. Wolery and R.D. Myser, 1974. Occurrence of As, Cd, Co, Cr, Cu, Fe, Mg, Ni, Sb and Zn in Lake Erie sediments. In: Proc. 17th Conf. Great Lakes Res., pp. 219-234.
- Yasuno, M., S. Hatakeyama and Y. Sugaya, 1985. Characteristic distribution of chironomids in rivers polluted with heavy metals. Int. Verein. Limnol., 22: 2371-2377.



TOTAL AND EXTRACTABLE HEAVY METAL CONTENT OF SOME SOILS OF THE LUBLIN COAL MINING REGION

TADEUSZ FILIPEK

Department of Agricultural Chemistry, Agricultural Academy of Lublin, Lublin (Poland)

LUCJAN PAWLOWSKI

Department of Water and Wastewater Technology, Technical University of Lublin, 20-618 Lublin (Poland)

ABSTRACT

Increasing concentrations of total and extractable heavy metals (Ni, Pb, Cu, Zn and Mn) were found with increasing silt-clay fraction and organic carbon content of soils. Soluble forms of these metals were extracted from soils using solutions of 0.5 M HCl, 0.5 M CH₃COOH and 0.04 M Na-EDTA. The amount of extracted metals decreased generally in the order: HCl > EDTA > CH₃COOH. However, in many cases the EDTA solution extracted more Cu and Mn than the hydrochloric acid solution.

INTRODUCTION

Forms of heavy metals in soils determine their rate of circulation and migration to particular components of the environment such as water and biota [1–5]. The total content of an element in a soil determines only its potential for migration [6–8]. The content of extractable forms of heavy metals in soils is a more precise index of their ability to migrate [1, 2, 5]. The mobility of elements in soils depends on many factors, for example the cation sorption capacity, which is dependent upon clay mineral content, humus, aluminum and iron hydroxide, as well as pH and redox properties [2, 5, 8].

An aim of this investigation was to determine total and extractable forms of Ni, Pb, Cu, Zn and Mn in selected soils from the Lublin Coal Mining Region.

METHODS

The soil samples investigated were taken from the humus horizon of five areas around the Bogdanka coal mine (see Fig. 1): (A) Turka, (B) Rogóźno, (C) Piaseczno, (D) Bogdanka, and (E) Głębokie. Fifteen soil samples were taken at each site. Some properties of the soils are shown in Table 1.

The following solutions were used to extract the various forms of soluble heavy metals from the soil samples: 0.5 M HCl, 0.5 M CH₃COOH and 0.04 M Na-

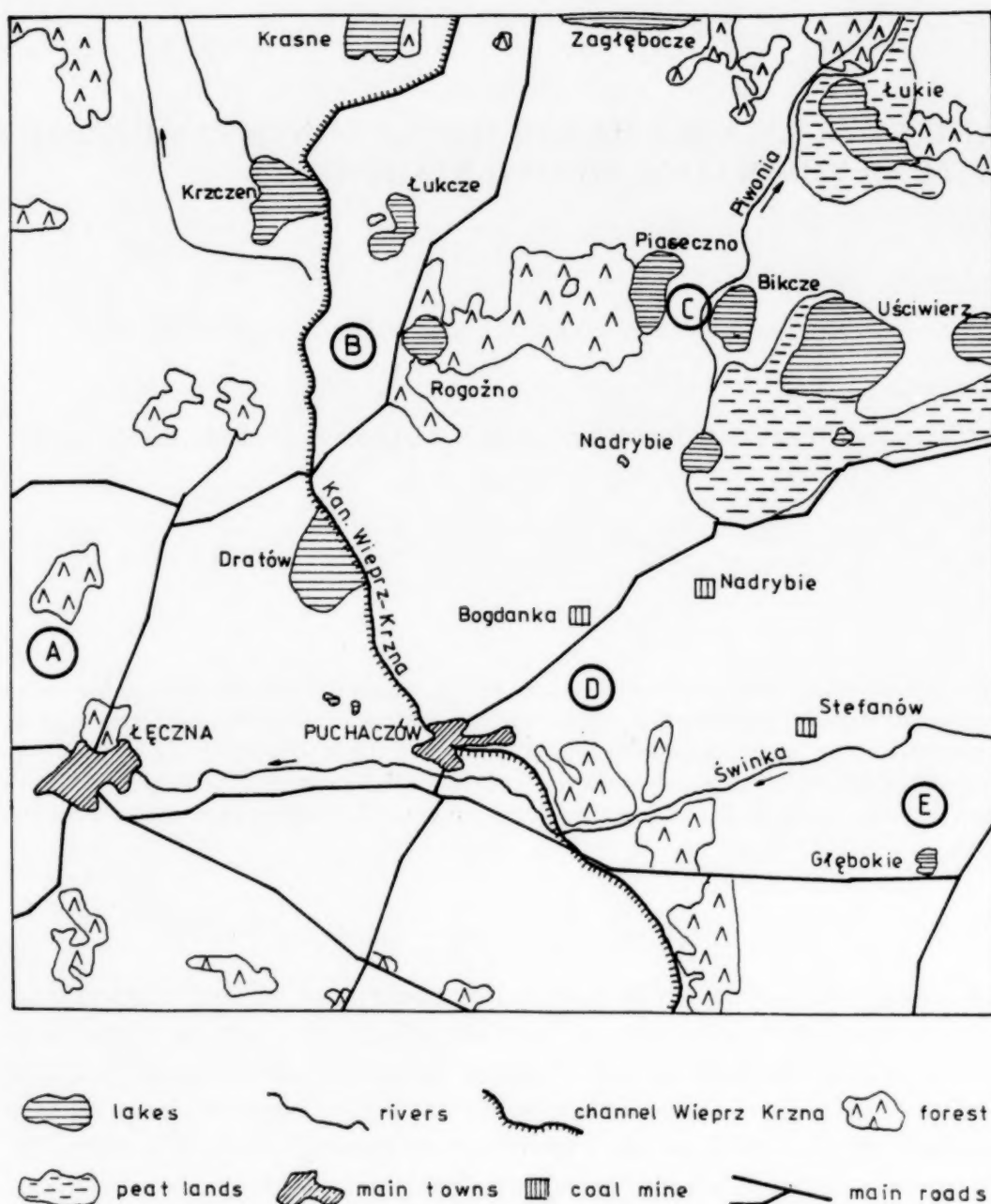


Fig. 1. Geographical characteristics of the sampling sites.

EDTA. Samples were mixed in a ratio of 1:10 (soil:solution) and shaken for 1 h in a laboratory mixer. The content of Zn and Mn was determined in the aqueous phase, while that of Ni, Pb and Cu was determined in the organic phase after complexation with ammonium pyrrolidinedithiocarbamate (APDC) followed by dissolution of the complex in methyl-isobutyl ketone (MIBK). An atomic absorption spectrometer (Pye Unicam SP-9) was used for the analysis of extractable metal concentrations. The total heavy metal content of the soils was determined by spectral emission analysis.

TABLE 1

Some properties of the soils^a

Site	Fraction (%)			PH in KCl	Organic carbon (%)	Hydrolytic acidity (mmol H ⁺ / 100 g)	CEC ^b (mmol/100 g)
	1-0.1 mm	0.1-0.02 mm	< 0.02 mm				
A	72 (57-91)	18 (6-27)	10 (3-16)	5.6 (4.8-6.9)	0.65 (0.38-0.87)	2.00 (0.74-3.62)	4.54 (3.24-6.48)
B	30 (18-47)	42 (31-56)	28 (16-40)	5.0 (4.2-6.4)	1.18 (0.72-1.66)	4.36 (3.34-4.85)	7.34 (4.23- 12.62)
C	78 (64-95)	15 (3-20)	8 (2-14)	4.5 (3.9-5.2)	0.69 (0.41-0.92)	3.54 (2.81-4.12)	3.82 (2.98-5.16)
D	22 (14-40)	50 (32-71)	28 (19-46)	4.9 (4.2-5.6)	1.03 (0.70-1.41)	4.08 (3.20-4.83)	7.86 (5.44- 10.42)
E	25 (18-31)	48 (30-52)	27 (19-42)	4.5 (3.9-5.5)	1.02 (0.85-1.30)	4.98 (3.64-5.30)	6.49 (4.82-9.54)

^a Average values with range in parentheses^b CEC, cation exchange capacity.

RESULTS

The total heavy metal concentration in soils correlated mainly with the soil texture and humus content (Table 2). The lowest quantities were found in soil from Site C, which is strongly acidified and consist of coarse sand. In the parent sandy rock, consisting mainly of quartz particles which are not susceptible to weathering, there has been little deposition of organic matter, and thus there was no accumulation of elements during podzolization.

In the soils formed from silt, high concentrations of elements occurred due to greater sorption capacity and lower acidification, making leaching less favorable.

The extraction solutions used in these investigations released various quantities of metals from the soils (Table 3). The HCl solution extracted the greatest amounts of Ni, Pb and Zn from the soils at all sites. Smaller amounts of metals were released when EDTA was used, and the smallest amounts were released by extraction with CH_3COOH . For Cu and Mn, the amounts released from the soils of Turka, Rogóžno and Piaseczno by the strongly complexing EDTA extraction solution were higher than when HCl was used.

The amounts of heavy metals extracted from the soils depended upon soil type and the properties of the extraction agent (Table 4). Generally, the amount of element released from a coherent soil of high organic content was greater than that from a more sandy soil. The lowest metal contents were found in soil from Site C. This was probably due to either leaching of those elements and/or lower content in the parent rock. At low pH, extractability increased considerably and the organic and mineral colloid binding force decreased, which in turn promoted metal leaching through the soil.

Table 4 presents correlation coefficients between the percent content of silt and clay, organic carbon, pH and acidity and the amount of extractable heavy metals in the soils. The content of extractable Ni was positively correlated to the quantity of silt in the soils. The highest correlation was found for hydrochloric acid. Similarly, statistically significant r_{xy} coefficients were found for the amounts of extractable forms of Ni and the organic carbon content.

TABLE 2

Concentrations of total heavy metals in the soils^a (mg kg^{-1})

Site	Ni	Pb	Cu	Zn	Mn
A	8 (4-18)	12 (7-23)	16 (12-30)	26 (19-60)	135 (85-350)
B	16 (6-32)	14 (5-26)	19 (13-40)	38 (24-65)	196 (103-540)
C	5 (3-8)	8 (3-10)	9 (4-12)	19 (11-24)	78 (32-90)
D	21 (16-27)	27 (15-32)	23 (7-46)	44 (30-82)	334 (145-520)
E	19 (8-29)	16 (11-22)	18 (11-36)	33 (23-50)	262 (116-394)

^a Average values with range in parentheses.

TABLE 3

Concentrations of extractable heavy metals in the soils^a (mg kg⁻¹)

	Extraction solvent	Site				
		A	B	C	D	E
Ni	HCl	1.1 (0.2–2.0)	1.3 (0.3–3.1)	0.5 (0.0–1.2)	1.5 (0.4–3.5)	0.8 (0.0–1.9)
	CH ₃ COOH	0.4 (0.0–0.9)	0.6 (0.0–1.2)	0.2 (0.0–0.8)	0.6 (0.0–1.5)	0.2 (0.0–0.8)
	EDTA–Na	0.7 (0.3–2.3)	1.0 (0.2–1.9)	0.2 (0.0–0.6)	0.7 (0.2–2.1)	0.5 (0.0–1.3)
Pb	HCl	5.3 (1.6–8.4)	6.4 (1.3–12.4)	5.7 (2.6–7.2)	6.3 (1.8–12.3)	5.6 (1.3–9.7)
	CH ₃ COOH	0.2 (0.0–1.2)	0.5 (0.0–1.6)	0.7 (0.2–2.3)	0.2 (0.0–1.6)	0.4 (0.0–2.1)
	EDTA–Na	4.5 (0.3–8.2)	3.6 (0.8–8.2)	3.4 (0.8–6.1)	4.0 (0.8–6.4)	4.3 (1.6–5.6)
Cu	HCl	2.3 (0.6–4.9)	2.3 (0.6–4.8)	2.5 (0.4–3.8)	3.4 (0.3–6.1)	2.9 (1.1–4.2)
	CH ₃ COOH	2.1 (0.8–4.7)	2.1 (0.7–5.0)	2.1 (1.2–3.8)	2.1 (1.2–4.0)	2.1 (0.6–3.1)
	EDTA–Na	2.5 (1.2–3.8)	2.8 (1.3–4.7)	2.5 (1.4–4.6)	3.2 (1.6–5.3)	2.6 (1.2–4.8)
Zn	HCl	5.4 (2.6–8.9)	14.6 (6.2–24.7)	2.6 (1.4–6.3)	7.5 (2.6–11.3)	4.3 (2.1–6.8)
	CH ₃ COOH	3.1 (1.6–7.2)	9.0 (2.0–21.3)	2.0 (0.3–3.6)	3.8 (1.4–5.6)	2.4 (1.2–4.5)
	EDTA–Na	3.8 (2.2–8.1)	10.9 (3.2–22.6)	1.5 (0.7–2.3)	5.5 (2.2–8.3)	3.5 (2.1–5.2)
Mn	HCl	65.0 (36.4–102.3)	136.0 (64.2–237.2)	38.7 (12.6–59.4)	135.6 (34.5–260.3)	82.6 (31.4–114.5)
	CH ₃ COOH	18.8 (9.4–47.6)	34.7 (18.2–74.3)	19.4 (10.3–42.4)	40.0 (12.4–81.3)	34.7 (19.6–58.2)
	EDTA–Na	79.1 (26.4–107.4)	140.3 (74.4–240.3)	47.0 (18.7–72.3)	114.3 (64.5–311.0)	92.4 (31.8–165.2)

^a Average values with range in parentheses.

TABLE 4

Correlation coefficients (r_{xy}) between some soil properties and extractable heavy metal content

Soil property	Ni			Cu			Mn		
	HCl	CH ₃ COOH	EDTA	HCl	CH ₃ COOH	EDTA	HCl	CH ₃ COOH	EDTA
Silt and clay content	0.73*	0.65*	0.66*	0.43	0.00	0.64*	0.86**	0.80**	0.78**
Organic carbon content	0.54	0.55	0.52	0.29	0.16	0.66*	0.68*	0.65*	0.58
pH	0.22	0.00	0.21	-0.13	-0.14	-0.31	0.02	-0.29	-0.09
Acidity	0.12	0.23	0.09	0.21	0.49	0.07	0.51	0.27	0.91**

* Significant correlation ($p = 0.05$), ** highly significant correlation ($p = 0.01$).

A significant correlation coefficient was obtained for the quantity of Cu extracted with EDTA solution and the organic carbon content, indicating that a considerable amount of Cu is extracted by the EDTA solution. A slightly smaller, but significant correlation coefficient was found between the content of the smallest soil particles and Cu extracted with EDTA.

The amount of Mn extracted with the solvents investigated was highly positively correlated with the content of silt and clay, organic carbon and acidity.

CONCLUSIONS

(i) The contents of total and extractable, i.e. ecologically significant, forms of nickel, copper and manganese in investigated soils were positively correlated with texture, organic carbon content and, to a smaller degree, acidity.

(ii) The amount of heavy metals released from soils on extraction by different solutions generally decreased as follows: HCl > EDTA > CH₃C-OOH. However, in the case of copper and manganese, the strongly complexing EDTA often extracted more of these metals than the HCl solution.

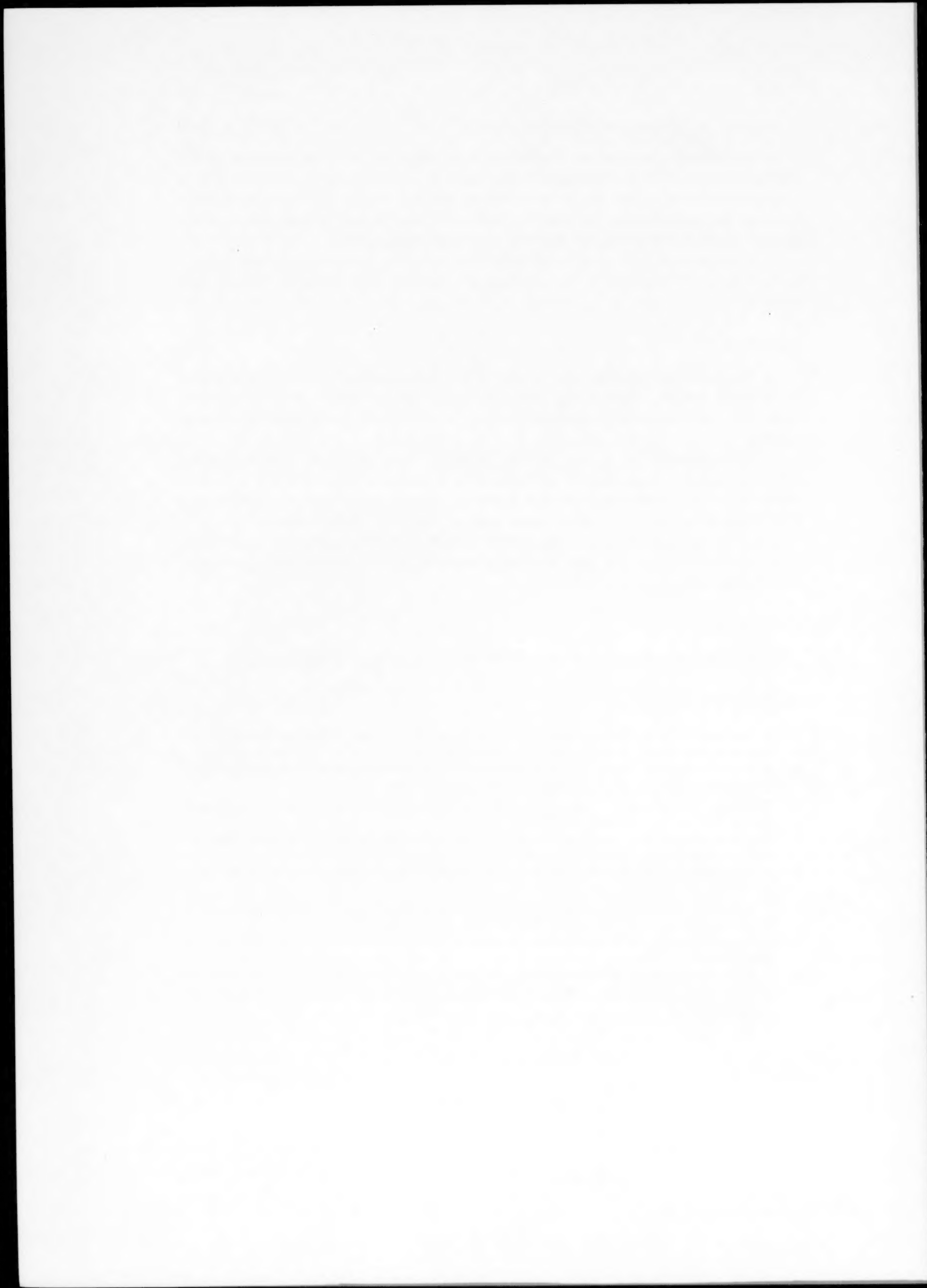
(iii) The amount of copper extracted with EDTA was positively correlated with organic carbon content, while the amount of manganese was positively correlated with acidity.

ACKNOWLEDGEMENT

Financial support under grant CPBP 04.10.16. is fully acknowledged.

REFERENCES

1. A. Anderson, On the determination of the ecologically significant fraction of some heavy metals in soils, *Swed. J. Agric. Res.*, 6 (1976) 19-25.
2. R.J. Haynes and R.S. Swift, Effects of soil acidification and subsequent leaching on levels of extractable nutrients in a soil, *Plant Soil*, 95 (1986) 327-336.
3. A. Kabata-Pendias and H. Pendias, *Pierwiastki śladowe w środowisku biologicznym*, Wydawnictwa Geologiczne, Warszawa, 1979.
4. K.S. Maclean and W.M. Iangille, Extractable heavy metals in Atlantic coast soils, *Commun. Soil Sci. Plant Anal.*, 11 (1980) 1041-1049.
5. L. Wiklander and K. Wahtras, Solubility and uptake of heavy metals from a Swedish soil, *Geoderma*, 19 (1977) 123-129.
6. J. Dudas and S. Pawlus, Trace elements in sewage sludges and metal uptake by plants grown on sludge-amended soil, *Can. J. Soil Sci.*, 2 (1975) 239-243.
7. A. Kabata-Pendias, Zawartość metali ciężkich w glebach Polskich, *Pamięt. Puławski*, 74 (1981) 101-111.
8. R. Turski and S. Baran, Zawartość Pb, Zn, Cu, Mn, B, Ni i Sr w różnych typach gleb w rejonie oddziaływania huty cynku — Miasteczko Śląskie, *Zesz. Probl. Postępów Nauk Roln.*, 179 (1976) 609-625.



ASSESSMENT OF ALUMINIUM MOBILIZATION AND PATHWAYS IN THE BIRKENES CATCHMENT, SOUTHERN NORWAY

ROLF VOGT¹, HANS MARTIN SEIP¹, NILS CHRISTOPHERSEN² and SJUR ANDERSEN¹

¹*Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, Oslo 3 (Norway)*

²*Center for Industrial Research, P.O. Box 124, Blindern, Oslo 3 (Norway)*

ABSTRACT

In spite of considerable research efforts the detailed mechanisms involved in acidification, and in particular those controlling aluminium concentrations in water, have not been satisfactorily established. In this paper, earlier work on acidification carried out in the Birkenes catchment in southern Norway is first reviewed. Temporal variations in acidity and aluminium concentrations in stream water are related to variations in ionic loadings. Addition of sodium bromide to two small soil plots in Birkenes resulted in high concentrations of H^+ in the organic horizon and of Al^{3+} in the eluvial horizon. The experiment supports the hypothesis presented earlier that water pathways are of great significance in determining stream water chemistry. Suggestions for the improvement of existing models for calculating stream water aluminium concentrations are given.

INTRODUCTION

Long-term deposition of acidity and sulphur compounds (SO_4^{2-} , SO_2) has been identified as the principal cause of acidification of surface waters and increased mobilization of aluminium from edaphic reservoirs to adjacent surface waters [1–3]. Many of the important processes are known. The increase in sulphur deposition results, for example, in an increase in the concentrations of sulphate in surface waters. This must necessarily lead to higher concentrations of cations including H^+ and aluminium ions if the soil is acid [3,4]. A number of investigations has shown that there is a seasonal variation in the acidity of rivers and lakes, with the most acidic periods usually observed during snowmelt and in the autumn, particularly when heavy rain occurs after a dry summer (cf. [3]). This is related to high ionic concentrations in stream and soil water during these periods (cf. [5] and [6]).

However, in spite of considerable research efforts the detailed mechanisms involved in acidification, and in particular those controlling aluminium concentrations in surface waters, have not been satisfactorily established [7–11]. Studies of precipitation, stream water, and soil water in small catchments have been used extensively to clarify the important mechanisms in water acidification. At the Birkenes catchment in southernmost Norway (Fig. 1), precipitation and water chemistry have been investigated since 1971–1972 by the Norwegian

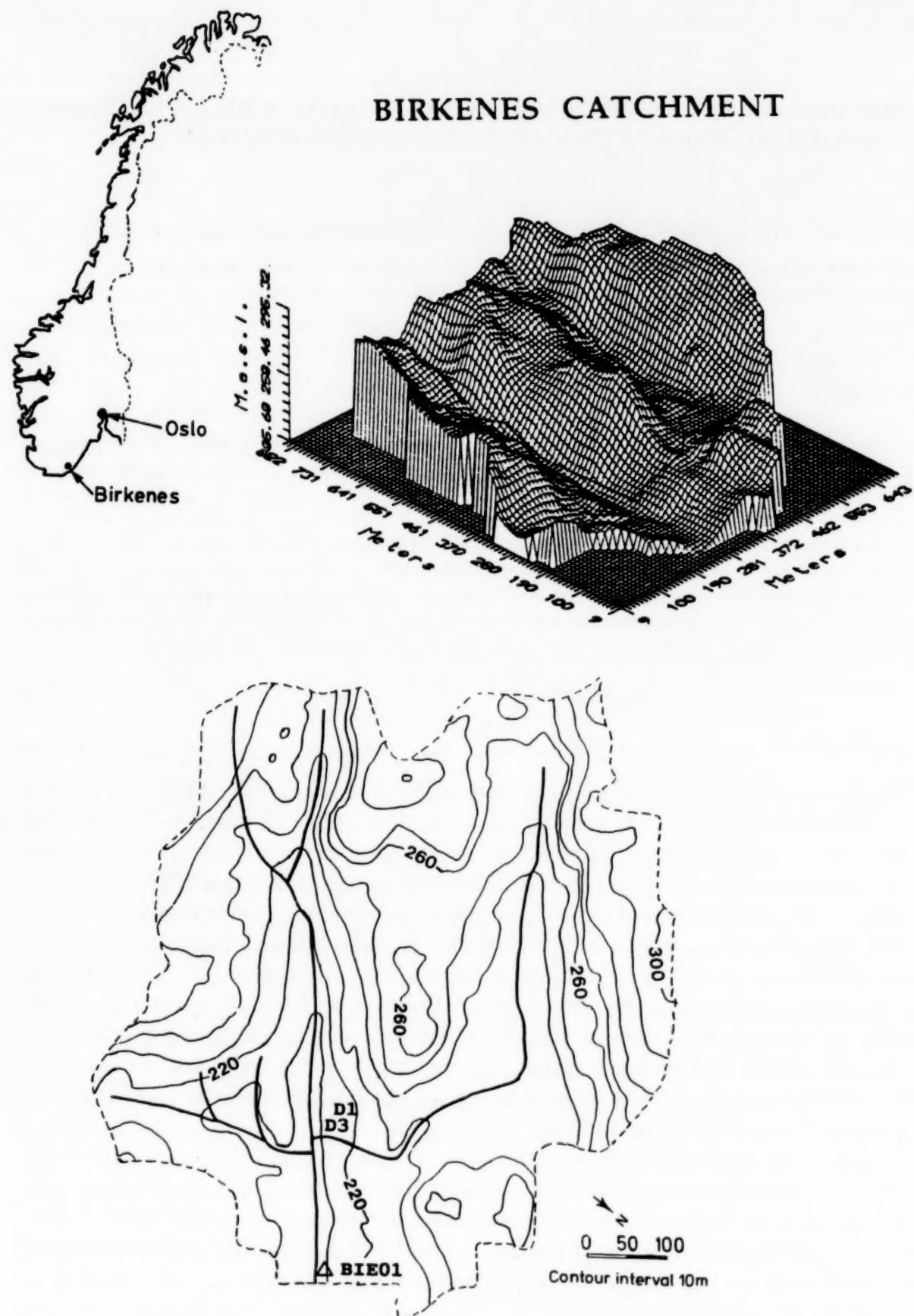


Fig. 1. Location in Norway; three-dimensional view and topographic map of Birkenes catchment with stream sampling locations (BIE01) and salt addition plots (D1, D3).

Institute for Air Research (NILU) and the Norwegian Institute for Water Research (NIVA), resulting in one of the longest data records of this kind in the world. In addition, intensive episode studies have been carried out since 1984 during spring snowmelt and autumn rainfall periods. Data from Birkenes have played an important role in the discussion of causes of water acidification.

The observations clearly show that the acidity of stream water is positively correlated to discharge. Rosenqvist [12] emphasized that the amount of precipitation determines, to a large extent, the acidity of the discharge (cf. [13]). When considering only a short time scale, such as hours or a few days, this dependence may be explained by changes in water pathways. At high discharge, most of the water passes only through the upper, acid soils before entering the stream. The importance of water pathways in the chemistry of stream water has been confirmed by other studies [8, 11, 14, 15].

Christophersen et al. [16] regarded stream water as a mixture of selected soil water classes or "endmembers". They presented a technique to estimate the contributions from each endmember at all times when stream water samples are taken. At the present state of development the composition of the endmembers is assumed constant. Soil water data show that this approximation is better for deeper rather than for upper soil layers. A study by Mulder et al. [17], carried out during and after a storm event with extremely high deposition of seasalt, showed considerable variations in the composition of soil water in the O/H and E layers. The same was observed by monitoring the soil solution chemistry during transition from dry to wet conditions. To study the variation in endmember composition further, a salt (NaBr) was added to two small soil plots at Birkenes. Both chloride and bromide are suitable as water tracers in Birkenes soils, but we decided to use NaBr since the natural background of Br^- is below the detection limit. The results will be presented here, but we will first review previous work conducted at Birkenes.

SITE DESCRIPTION

The Birkenes catchment (Fig. 1) is a small (0.41 km^2) watershed located at $58^\circ 15' \text{N}$, $08^\circ 15' \text{E}$ in the region of highest sulphur deposition in Norway ($\sim 6 \text{ g SO}_4 \text{ m}^{-2} \text{ year}^{-1}$ [27]). Vegetation is dominated by Norway spruce. The elevation ranges from 185 to 275 m above sea level. Below an organic or humic layer ($\sim 10 \text{ cm}$) are shallow mineral soils ranging from true podzol (spodosols) to acid brown earths which have developed into a layer of glacial till overlaying granitic bedrock. The mineral soil depth generally decreases with increasing elevation from ~ 1 to 0 m. In the valley bottom an extensive area around the brooks is covered by soligenous bogs (0.1–2.5 m deep), comprising 7% of the total catchment area [18].

Birkenes has a humid climate with an average precipitation of $\sim 1370 \text{ mm year}^{-1}$ (Table 1). Rain is registered on about 50% of the days, and during the summer months evapotranspiration usually exceeds precipitation, resulting in summers with little discharge; the autumns are generally wet with high discharge.

TABLE 1

Average volume-weighted concentrations ($\mu\text{eq l}^{-1}$, except where indicated) of major ions in precipitation and streamwater at Birkenes (1973–1978, 1981–1983 and 1985–1987) [38]

		Precipitation BIN01	Streamwater BIE01
Water	(mm)	1370	1067
H ⁺		54	30
Na		52	114
K		4	6
Ca		9	58
Mg		13	36
NH ₄		40	— ^a
SO ₄		68	145
Cl		56	125
NO ₃		38	8
Total Al	(μM)	— ^a	21

^a— not measured; presumably very small.

ALUMINIUM – ANALYTICAL METHODS AND CONTROLLING MECHANISMS

In addition to the ionic form, $\text{Al}_{(\text{aq})}^{3+}$, aluminium in soil and surface waters may exist in a number of complexes with inorganic (e.g. OH^- , F^-) or organic ligands. To discuss aluminium chemistry, a distinction must be made between aluminium species. Following Barnes [19] and Driscoll [20], we have first made a separation into “polymeric” and “monomeric” forms. By using a cation exchange column the monomeric fraction is separated into mainly inorganic monomeric “labile aluminium (Al_i)” and organically complexed monomeric “non-labile aluminium (Al_o)”. Further speciation of Al_i was carried out using ALCHEMI, a computer program developed by Schecher and Driscoll [21], assuming equilibrium of dissolved species with OH^- , F^- , or SO_4^{2-} as ligands, but no AlSi complexes. A detailed description of sample treatment and analytical procedures has been reported by Sullivan et al. [22].

A simple equilibrium with an aluminium trihydroxide was suggested by Magistad [23] as the major mechanisms controlling aluminium concentrations in soil waters:



implying the following solubility relationship:

$$[\text{Al}^{3+}]/[\text{H}^+]^3 = K_s. \quad (2)$$

For synthetic gibbsite $[\text{Al}(\text{OH})_3]$, $K_s = 10^{8.1}$ at 25°C [24], increasing to $10^{9.3}$ at 5°C ; for amorphous $\text{Al}(\text{OH})_3$, the value is about 100 times greater.

Deviations from equilibrium with a given mineral will be discussed later in terms of the saturation index (SI),

$$SI = \log (Q_s/K_s) \quad (3)$$

where Q_s is the ion product and K_s the equilibrium constant (solubility product). SI is a standardized measure of the degree of saturation with respect to a specified mineral. Positive values indicate supersaturation while negative values show undersaturation.

Equation (2) also describes the relationship of a simple cation exchange reaction [25], though the value of K_s may then be lower than that corresponding to synthetic gibbsite [26]. Equation (2) has been assumed in most mathematical models simulating stream water concentrations in acidified catchments, though recent work, including studies at Birkenes [7, 11], has shown that the relationship is violated in many cases.

PREVIOUS STUDIES AT BIRKENES

Precipitation and stream water

Precipitation and stream water have been monitored at Birkenes since the beginning of the 1970s [3, 27]. Concentrations of major ions in precipitation and in stream water are given in Table 1. The pH of precipitation varies greatly from ~ 3.2 to ~ 6.2 , with a mean of 4.3. The pH typically increases through a storm event (cf. [28]). Major anions in precipitation are chloride and sulphate with average volume-weighted concentrations of 56 and 68 $\mu\text{eq l}^{-1}$, respectively.

The stream water in the main brook has a volume-weighted mean pH of 4.5. The surface waters are highly undersaturated with respect to all forms of gibbsite, $\text{Al}(\text{OH})_3$, at high discharge, but return gradually to saturation at low flow [11]. Dramatic elevations in the concentrations of inorganic aluminium and H^+ in the brooks are common during the first episode following an extended

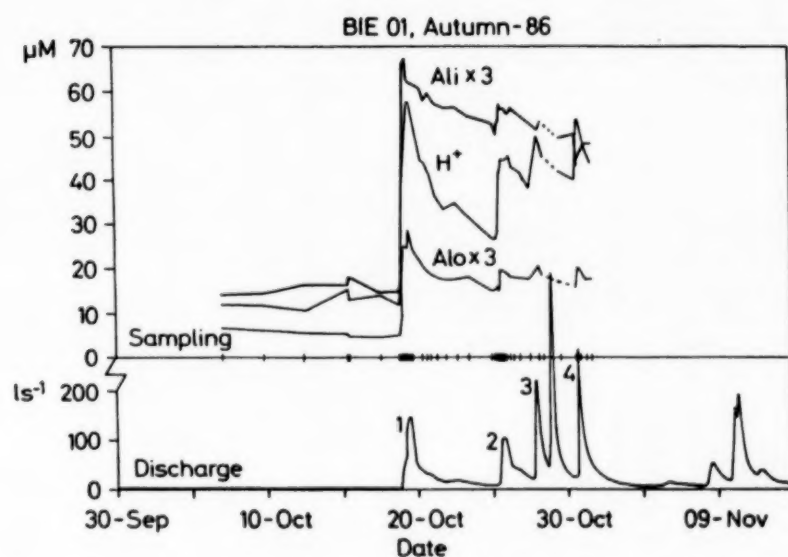


Fig. 2. Stream water discharge (l s^{-1}) and concentrations of H^+ , Al_i , and Al_0 for the autumn of 1986.

TABLE 2

Chemical characteristics of the various horizons of the two major soil types in the Birkenes catchment (Mulder et al. [17] or, marked with asterisks, Frank [29])

		Podzolized brown earth				Bog		
		O	E	Bhs	Bs	Of	Oh	C
pH (1:1.25 H ₂ O)		3.7*	4.2	4.7	4.8	3.7	4.2	5.1
Loss on ignition	(% w/w)	69.5*	3.0*	9.6*	0.8*	93.2*	64.9*	
Ca(ex)	(% CEC)		4.1	3.7	2.8	1.2	5.2	33.4
Mg(ex)	(% CEC)		2.1	1.5	1.2	0.4	0.5	6.1
Na(ex)	(% CEC)		< 2.2	< 1.8	< 1.8	< 0.4	< 0.5	< 8.4
K(ex)	(% CEC)		< 2.2	< 1.8	< 1.8	< 0.4	< 0.5	< 8.4
Al(ex)	(% CEC)		49.0	63.4	63.2	78.8	70.6	8.8
H(ex)	(% CEC)		43.9	29.9	32.1	19.6	23.7	49.4
CEC	(mmol kg ⁻¹)		47	59	61	245	194	15

Exchangeable base cations were determined in Li-EDTA at pH 7.0 and exchangeable H⁺ and Al in 1 N KCl extracts. The values are means of six samples.

low discharge period. While $[H^+]$ always shows a maximum at peak discharge, $[Al_i]$ (and $[Al^{3+}]$) though remaining high, may actually show small minima during subsequent events (see Fig. 2).

Soils

Soils at Birkenes have been studied by Frank [29] and by Mulder et al. [17]. Selected chemical characteristics for the two major soil profiles at Birkenes are given in Table 2.

The organic soil layers are generally acidic. The peat layers on top of the bogs have a large cation exchange capacity (CEC) and the major exchangeable cation is aluminium (CEC 245 mmol kg^{-1} , 78.8% is exchangeable aluminium). The mineral soil layers on the slopes are less acidic, with lowest pH in the E horizon (4.2) and higher values in the B horizon (4.7–4.8). Exchangeable acidity in the B horizons is dominated by aluminium. The cation exchange capacity of the soil is correlated with the amount of organic material.

Soil water

The soil water $[H^+]$ generally reaches the highest levels in the organic/humic layers and E horizons and typically decreases with depth, while the reverse trend was found for $[Al^{3+}]$ [11, 17, 28]. At Birkenes, pH values as low as 3.6 were found in the organic surface layers, while the highest pH (5.8–6.6) has been observed in the valley bottom below the bogs [30]. The saturation index with respect to gibbsite increased with pH; for synthetic gibbsite, SI varied from < -1 to ~ 1 , showing that the Al^{3+} concentration cannot be explained by solubility of one type of $Al(OH)_3$ [11].

There is a consistent trend of an abrupt rise in the water table through the soil profiles at the onset of storms. With the prevailing rain the water table shows a slower rising trend with frequent interception of organic deposits [8]. Mulder et al. [17] used a rain event with extremely high seasalt loading to study the effect on soil water chemistry and the importance of water pathways after an autumn storm when the catchment was at its hydrological field capacity. Monitoring the chloride pulse showed that precipitation inputs rapidly flowed laterally through the organic/humic horizons to the stream in nearly water-saturated soils. Vertical percolation of chloride-rich water was slow. Approximately 25% of the incoming rain reached the streams during the discharge event.

Mulder et al. [17] found that organic soil water approximately satisfied Eqn (2); the relationship between $[Al^{3+}]$ and $[H^+]$ was roughly cubic. The saturation indices with respect to all kinds of gibbsite were highly negative. It therefore seemed reasonable to assume that the aluminium and H^+ concentrations were determined by cation exchange in organic soils. Results of laboratory studies of the organic soils collected during the summer were consistent with this assumption. Exponents of ~ 3.1 were obtained for Eqn (2). However,

experiments on soils collected in the autumn gave an exponent of only 1.7 [30]. Similar low exponents for organic soil were also found by Bloom et al. [26].

The saturation index for mineral soil water was found by Mulder et al. [17] to be close to zero for synthetic gibbsite, but the exponent in Eqn (2) was < 3 . On the other hand, the laboratory studies [30] gave an exponent close to 3 both for summer and autumn samples. An aluminium-mineral dissolution mechanism is therefore a possible aluminium control in the mineral soil.

Modelling

A mathematical model has been used to simulate ionic concentrations in the Birkenes stream [31–33]. The model consists of two soil reservoirs and a snow reservoir when appropriate. For most ions the agreement with observed concentrations is good. However, aluminium presents a problem. In the original model, Eqn (2) was used in both soil reservoirs with the same value for K_s . Later, different constants were used for the two reservoirs, and an exponent of 2 has been tried for the upper one. These changes resulted in some improvements, but the agreement with observations is still not satisfactory. For example, the model has so far not reproduced observed high aluminium concentrations at the beginning of the snowmelt [31].

Christophersen et al. [16] developed a least-squares technique to estimate the contributions to the stream from a selected set of "endmembers"; EndMember Mixing Analysis (EMMA). The three major soil solution endmembers in Birkenes were considered to be the organic/humic surface layer (O/H), the podzol mineral soil (B/C) and the deep deposits in the valley bottom (VB). As a first approximation, the compositions of the endmembers were set constant in time.

Summary and conclusions based on previous studies

Seip et al. [11] suggested that different aluminium mechanisms in different soil layers combined with a change in water pathways with discharge qualitatively explained the observed stream water chemistry. This hypothesis was supported by Mulder et al. [17]. The Birkenes data are, in general, consistent with cation exchange reactions determining the concentration of inorganic aluminium in the organic soils, while the concentrations may be calculated assuming equilibrium with $\text{Al}(\text{OH})_3$ in mineral soils (cf. [9]).

A simulation model reproduces most major trends in discharge and stream water chemistry at Birkenes fairly well, indicating that many of the important processes are reasonably well represented in the model. However, the model still fails to reproduce finer details in the variations of stream water aluminium concentrations.

The EMMA concept may reduce scenario modelling of changes in surface water chemistry to long-term prediction of the fate of each endmember.

SALT EPISODES

The marine component of rainwater is fairly high in the Birkenes catchment due to its close proximity to the coast. As pointed out by Rosenqvist [12], and discussed by Skartveit [34], Wright et al. [6], and by Mulder et al. [17], high seasalt concentrations may significantly affect water chemistry primarily through cation exchange.

During the winter months, depositions of seasalts and anthropogenic pollutants accumulate in the snowpack at Birkenes. At the onset of spring melting, surges with high ionic strength originate from the snowpack due to the preferential leaching of the accumulated ionic load with the first meltwater [35] (cf. [28]).

During dry periods in the summer, pools of salts build up, particularly in the peat and on the vegetation. The sources for this summer salt pool may be the dry accumulation of aerosol sea-spray and anthropogenic pollutants, as well as a build-up of sulphate and soluble organic anions by degradation of organic matter. Such a salt pool was observed in a recent summer episode study of soil solution chemistry [39]. The data exhibit large temporal variations from dry to

CHEMICAL VARIATIONS IN ORGANIC SOILS

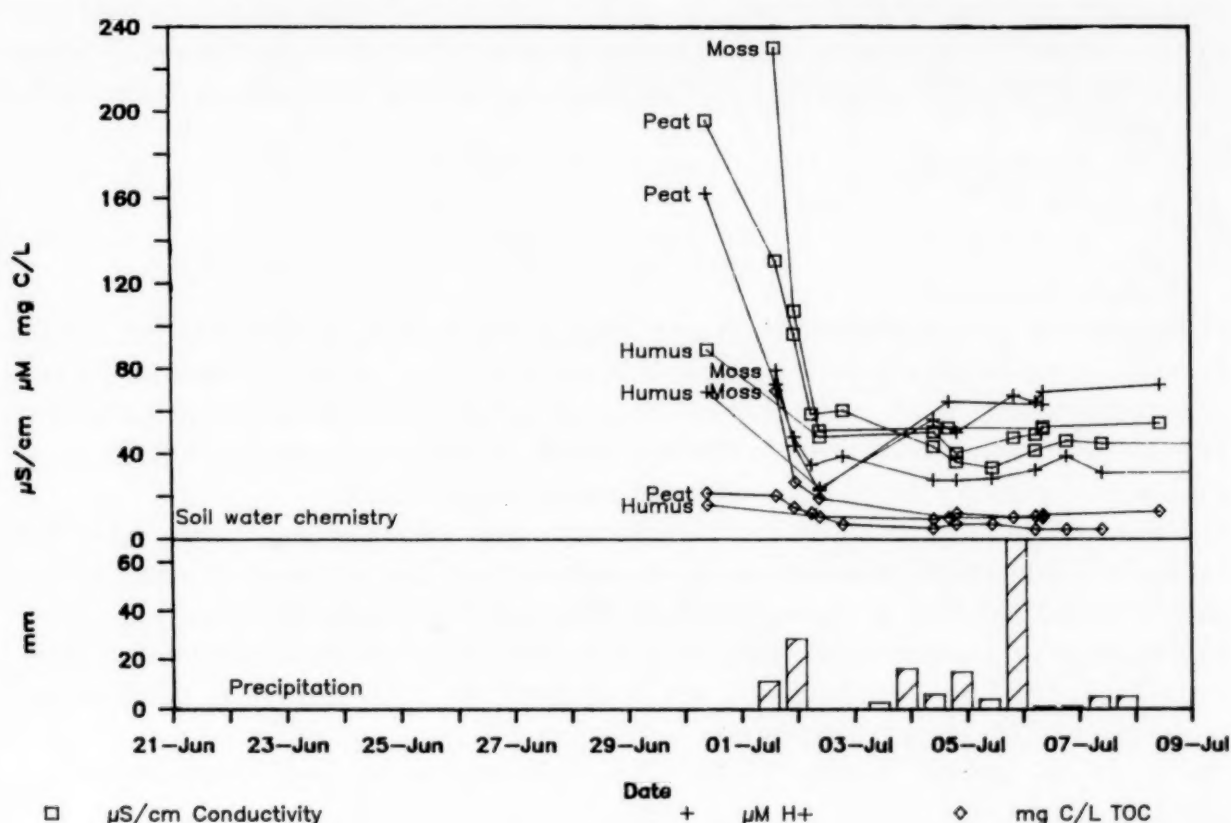


Fig. 3. Conductivity, $[\text{H}^+]$ and TOC in the humic, moss and peat horizons during a transition from a dry to a wet period in the summer of 1988. After 6 weeks practically devoid of rain, 40 mm fell on July 1st and 2nd.

wet conditions in sub-moss and peat layers, due to the outwash of a pool of ions from tree canopies and organic turf (Fig. 3). The variations were smaller in the H horizon eluates in the podzol profile, probably due to higher permeability and therefore frequent flushing and lateral water movement during previous light rain showers.

From a modelling viewpoint these large seasonal variations in the upper soil reservoir in the Birkenes model (cf. [31–33]), and in the O/H horizon endmember in the EMMA model [16], appear to be of significance when modelling the H^+ and aluminium concentrations in stream water. The mineral soil solution, referred to as the lower soil reservoir in the Birkenes model or B/C and valley bottom (VB) endmembers in EMMA, showed small temporal variations in $[H^+]$ and $[Al^{3+}]$, compared with variations found in stream water, despite sampling under quite varied hydrological conditions [11].

PRESENT STUDY – NaBr ADDITION

Christophersen et al. [16] in their EMMA model, combined only soil water with properties corresponding to the O/H, B/C and valley bottom soil layers to simulate surface water chemistry. As a first approximation they stated that the chemistry of the endmembers is constant. They further assumed that the E horizon does not contribute significantly to the stream. In order to examine these assumptions, and improve our understanding of water pathways and soil processes, we decided to study soil water flow and chemistry in two small plots after the addition of a neutral salt with an anion that presumably flows with the water.

Methods

Sample treatment

Immediate processing in an on-site laboratory consisted of determining pH, temperature, conductivity, UV absorption [for total organic carbon (TOC) estimation], and fractionation and determination of monomeric aluminium. Due to small sample volume (< 300 ml), dilution prior to aluminium fractionation was necessary for the majority of samples collected.

Bromide was analyzed by ion chromatography (Waters ILC1). We used the bromide concentration as an accurate measure of the amount of salt in the solution and the soil water movement. The specific conductivity of solutions was used as an indicative substitute parameter where bromide concentrations were lacking. The sampling efficiency of the cup lysimeters was used as an indication of the soil hydrological condition.

Field study

In the autumn of 1988, salt (NaBr) was added in situ to two 4 m^2 natural soil plots, a podzol profile and a soligenous peat. These are the two major soil types in the Birkenes catchment (covering 79 and 7%, respectively [18]) that are

TABLE 3

Lysimeter depth and soil horizon in podzol and peat plot

Lysimeter	Plot	Horizon	Depth (cm)
Cup lysimeter 10	D (1)	Humic (H)	- 8
Cup lysimeter 11	D (1)	Eluvial (Ea)	5
Cup lysimeter 12	D (1)	Eluvial (Ea)	4
Cup lysimeter 13	D (1)	Illuvial humus (Bhs)	17
Cup lysimeter 14	D (1)	Illuvial iron (Bs)	23
Cup lysimeter 15	D (1)	Parent material (Bs/C)	32
Cup lysimeter 21	D (3)	Partly decomposed (Of)	- 45
Cup lysimeter 22	D (3)	Well decomposed (Oh)	- 25
Cup lysimeter 23	D (3)	Parent material (C)	1

considered to affect surface water chemistry during high flow. A total of 12.5 mm of a 5.0 mM solution of NaBr was added over a 2 h period. This amounted to a total addition of 62.5 meq m⁻² of bromide. The main monitoring period lasted 16 days. Later samples were collected after major precipitation episodes 29 and 37 days after initiation.

Two adjacent sites (podzol and peat) were selected on the southeast-facing slope of the main brook (Fig. 1). The podzol profile is situated on a gentle slope. It is 50 cm deep, with a 10 cm thick humic layer and a 13 cm deep E horizon. The peat profile is situated in a concavity on the slope. It consists mainly of 50 cm deep turf with a 2 cm sandy layer at the bottom overlying the granitic bedrock.

The soil solution chemistry in the different horizons was monitored by means of ceramic cup suction lysimeters for constant soil water sampling (655X1-B1M3, Soil Moisture Corp., Santa Barbara, CA) using a non-constant tension of max. 50 kPa. Details of lysimeter installations are given in Table 3.

Results

Variations in concentrations of Br⁻ for the podzol and peat profile are given in Fig. 4. TOC, [Al³⁺] and [H⁺] are shown in Figs 5 and 6 for the podzol and peat profile, respectively.

In the humic horizon of the podzol there was an almost immediate increase in [Br⁻] accompanied by a dramatic increase in [H⁺]. There was some increase in [Al³⁺], but the concentrations remained moderate. When the soil became wet after the event on Days 13 and 14, there was a slight increase in [H⁺], but essentially no change in [Al³⁺]. In the E horizon the immediate response was small, but the event on Days 13 and 14 gave a dramatic increase in [Al³⁺]. The maximum concentrations measured were ~280 µM in lysimeter 12 and ~112 µM in lysimeter 11. These changes in the H and E horizons were presumably primarily due to H⁺ or aluminium ion-exchange with Na⁺. The concentrations decreased quite rapidly, probably due to mixing with lateral flow water. In the E horizon the mean SI was negative even with respect to

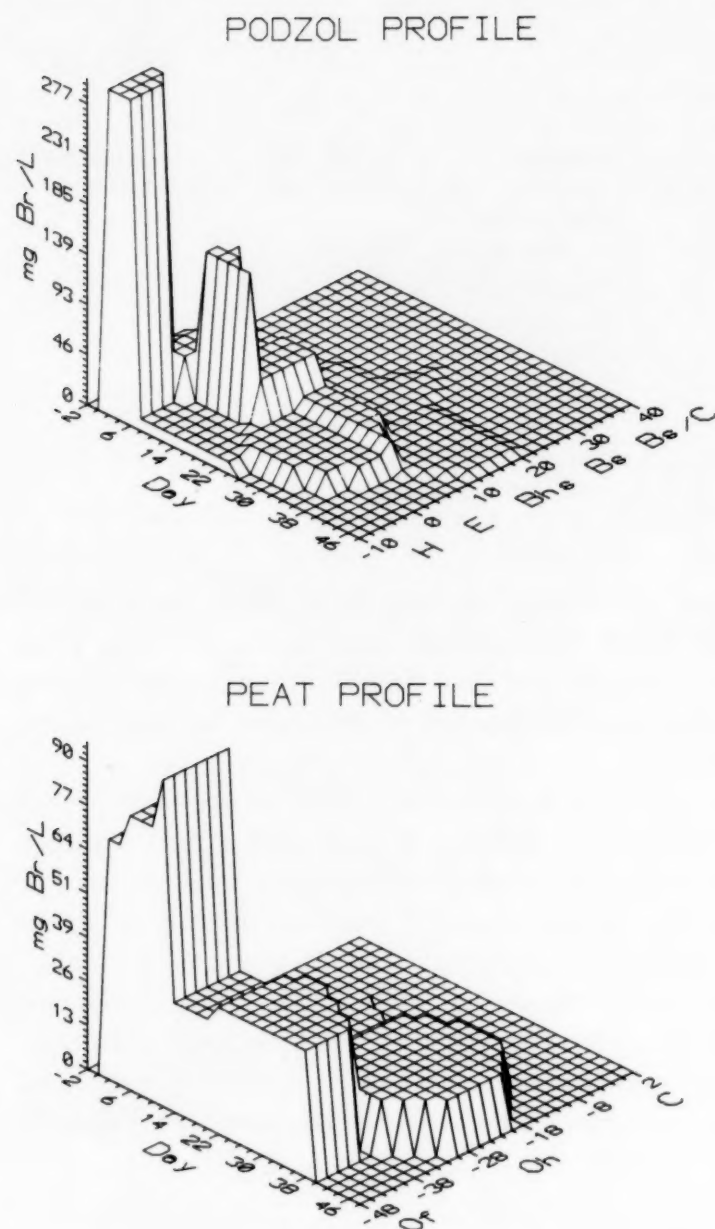


Fig. 4. Three-dimensional plots of soil water $[\text{Br}^-]$ vs time and the sampling depth for the podzol and bog profiles. The plots are based on 18 and 11 data points, respectively.

synthetic gibbsite. Analysis of pAl^{3+} vs pH from both E horizon cup lysimeters gave no appreciable correlation ($r^2 = 0.09$). During stable hydrological conditions prior to the event on Day 13, SI increased to ~ 0.5 .

Deeper in the profile, Br^- concentrations above background values were observed after the event (on Days 13 and 14), but these were only minor elevations.

In the upper lysimeter of the peat profile, the salt addition immediately produced high $[\text{H}^+]$ and $[\text{Al}^{3+}]$. High Al^{3+} concentrations were also found after the event on Days 13 and 14 (max. $\sim 110 \mu\text{M}$) coinciding with a peak in $[\text{Br}^-]$. The large amounts of water stored in the peat profile caused enhanced dilution

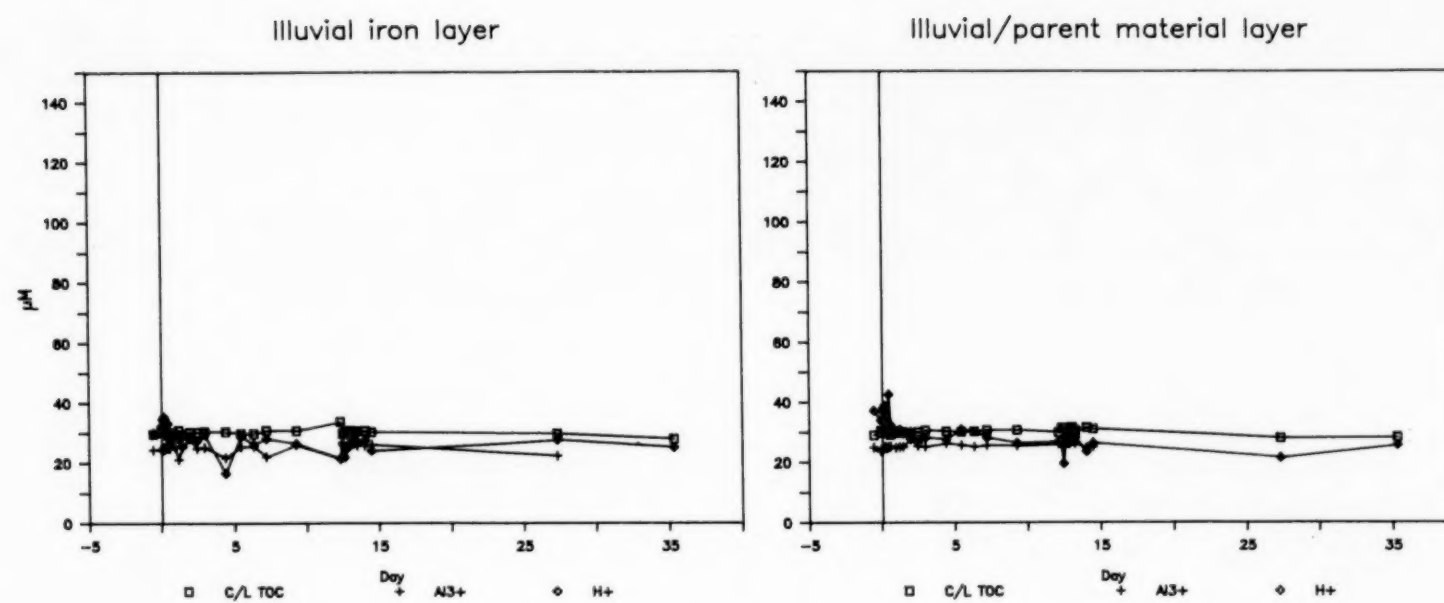


Fig. 5. Total organic carbon, $[Al^{3+}]$ and $[H^+]$ vs time at the different soil lysimeters in the podzol profile (cf. Table 3). TOC is given as μM carbon (continued on p. 152).

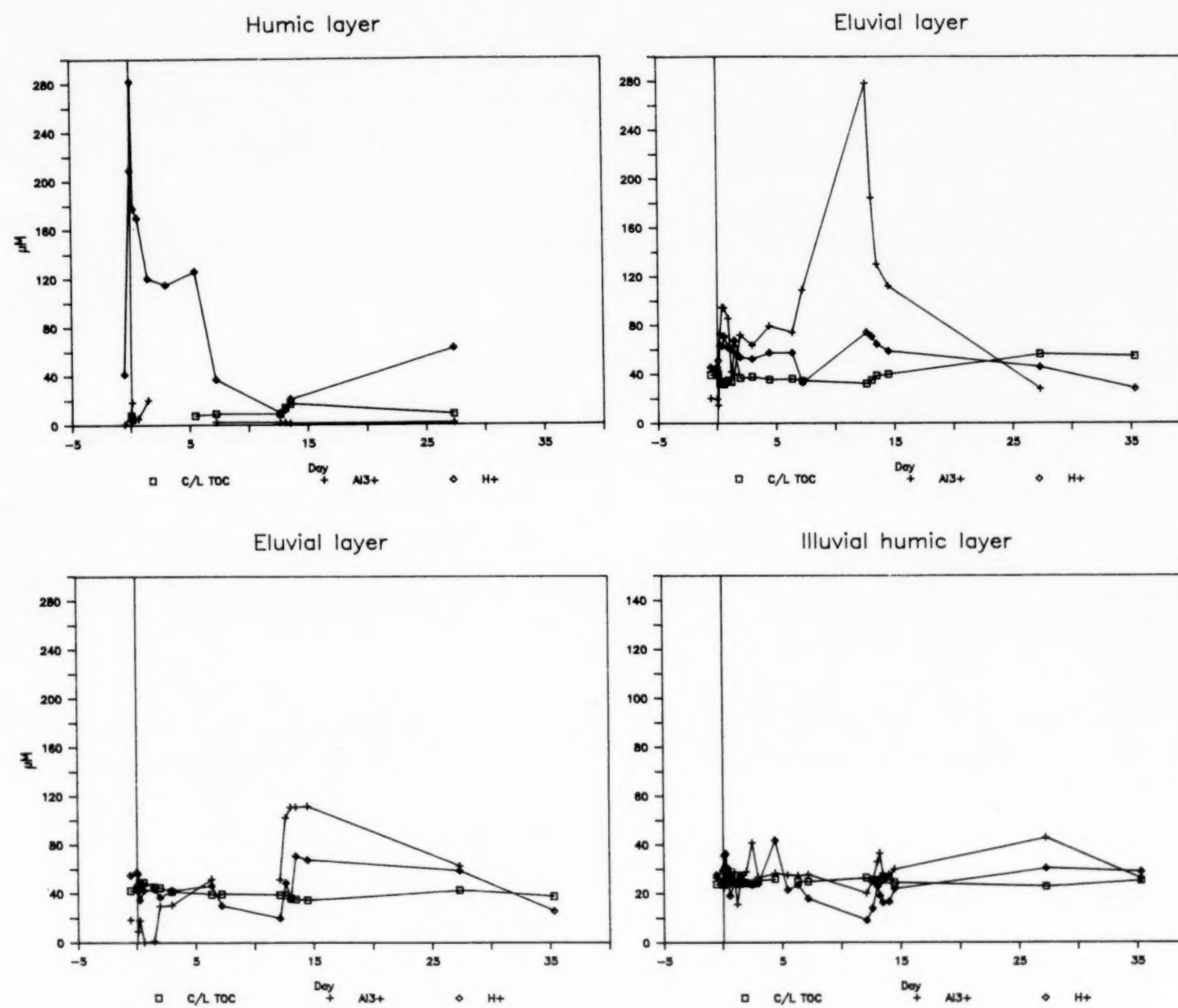


Fig. 5 (continued)

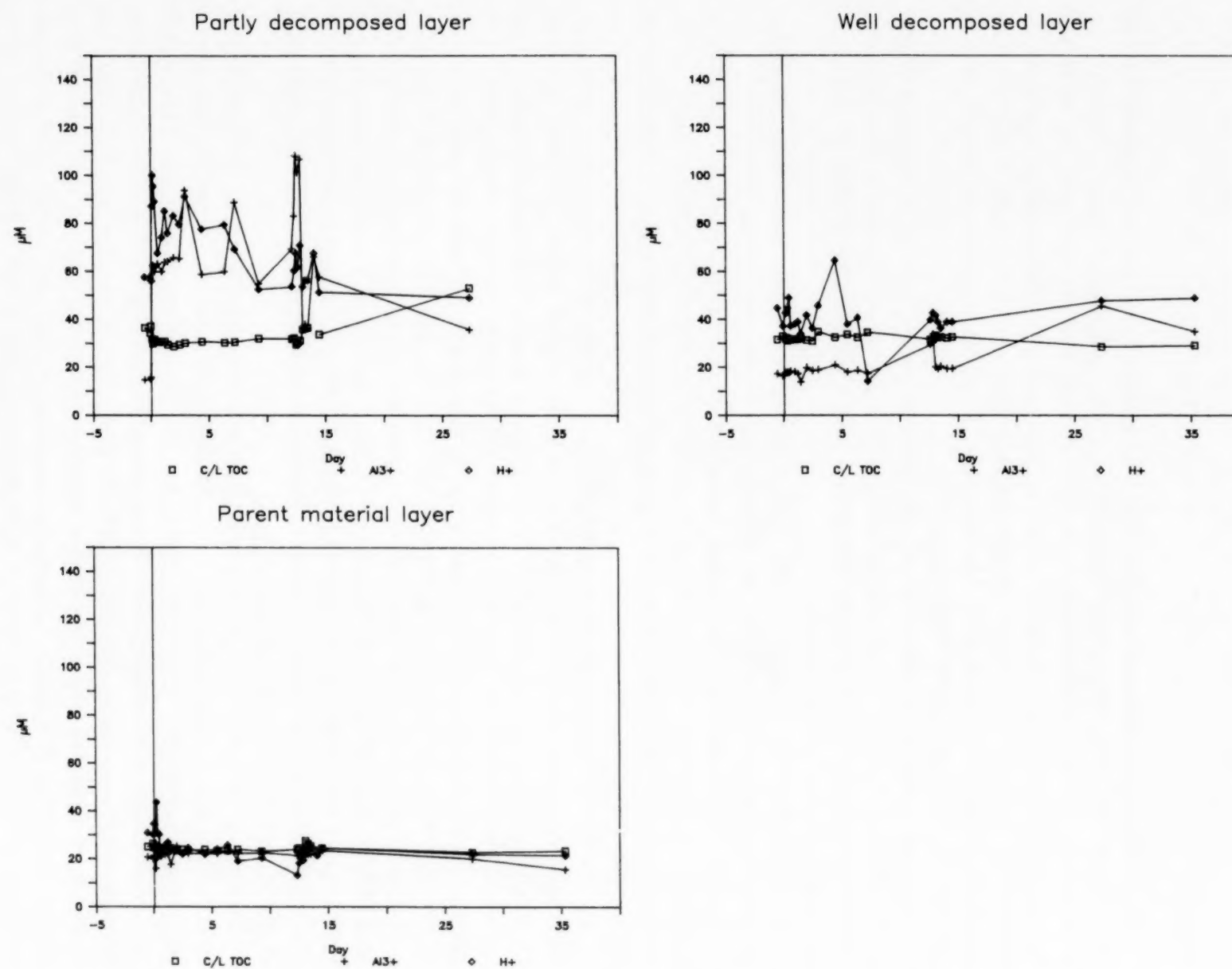


Fig. 6. Total organic carbon, $[\text{Al}^{3+}]$ and $[\text{H}^+]$ vs time at the different soil lysimeters in the peat profile (cf. Table 3). TOC is given as μM carbon.

of the added NaBr and thereby lower maximum salt concentrations than in the podzol. Further down in the profile the response was damped. In the mineral soil at the bottom of the peat profile we observed saturation indices close to zero with respect to synthetic gibbsite (ave. SI, 0.03).

DISCUSSION

The results are consistent with the hypothesis that ion exchange controls $[Al^{3+}]$ and $[H^+]$ in the water of organic soils and that mineral dissolution determines these constituents in water in the illuvial and parent material layers of mineral soils. The soil water chemistry in the eluvial layer is primarily controlled by ion-exchange reactions, though during stable hydrological conditions mineral dissolution may prevail. The water pathways are therefore critical for stream water chemistry.

The salt pulse resulted in high concentrations of H^+ in the H layer and particularly high Al^{3+} concentrations in the E layer. Under circumstances when lateral water-flow occurs, the pulses may cause highly acid and/or aluminium-rich water in the stream.

An hypothesized picture of the contributing soil water reservoirs, and the active flowpaths during different conditions, is presented below.

During dry conditions the water table is low. The main source of base flow is the water stored in deep soils and especially in organic deposits (bogs) in the valley bottom (VB). This water has a long residence time and is in equilibrium with gibbsite.

The primary response to a precipitation event is percolation of water through large pores down to the bedrock or water table. At deep profiles (≥ 20 cm) this water becomes neutralized and mixes with groundwater. The water table rises and a flow of B-horizon water to the stream may occur. This groundwater flow causes the discharge in the brook to respond within a few hours by forcing old down-slope water out into the stream, i.e. piston flow. The opening of this flowpath causes a shift from base flow conditions with pH 5.2 and $[Al^{3+}] \leq 2 \mu M$ to pH 4.5 and $[Al^{3+}]$ from 5 to $11 \mu M$. When the water table intercepts the E horizon, the water from the lower O/H and E horizons may be diverted by lateral flow through large pores in these horizons [36] and reach the surface waters directly (cf. [37]).

The chloride budget of the salt episode studied by Mulder et al. [17] indicated that, under the prevailing conditions, 20–30% of the water at Birkenes reached the stream so quickly that it had probably not passed the B horizon. This water was, therefore, not neutralized in the deeper layers, and negative saturation indices with respect to synthetic gibbsite in surface waters were observed. Our data show that the water from the humic/organic horizon is more acid, and water from the E horizon is more aluminium-rich, than water in the deeper mineral soil, resulting in further increase in acidity to pH 4.3 and $[Al^{3+}]$ up to $11 \mu M$ commonly observed in the stream during wet conditions.

A contributing factor is that the shallow soils are mainly situated at the

higher elevations farthest away from the streams. The precipitation that reaches these regions drains rapidly into the deeper soil profiles at lower elevations. This large flux of groundwater causes a billow on the groundwater table that moves rapidly down the hillslope. This wave sweeps the organic deposits on its journey and accumulates aluminium and hydrogen ions. The wave peak reaches the brook and causes maximum discharge 2–6 hours after the peak in precipitation.

During dry conditions a pool of easily mobilized salts will accumulate in the upper soils and on the vegetation due to dry deposition and small rainfall events followed by evapotranspiration. This pool will be mobilized by the first large rain event. Episodes high in salts will also occur at the beginning of snowmelt. During the winter months all deposited salts are stored in the snowpack.

The NaBr addition shows that such a pool of salts, when mobilized, may lead to dramatically elevated aluminium and hydrogen ion concentrations in the upper soil horizons. The observed lateral water flowpath may result in discharge from the organic and E horizons directly to the stream. The resulting stream water concentrations will depend on the relative amounts of water from these horizons. (The water in the H horizon has the highest $[H^+]$, the water in the E horizon the highest $[Al^{3+}]$.) This mechanism may explain the minimum pH values (~ 4.1) and/or maximum $[Al^{3+}] \geq 11 \mu M$ observed during the first event after antecedent dry conditions or at the beginning of snowmelt.

During periods of frequent precipitation (and thus saturated hydrological conditions), $[H^+]$ generally shows maxima at all discharge peaks. $[Al^{3+}]$, however, has only one clear maximum corresponding to the first storm event after a dry period. During later events, $[Al^{3+}]$ may even show a minimum. This may be explained by an additional rise of the water table into the organic deposits and discharge from the humic horizons with elevated $[H^+]$ without contact with mineral soil [8]. After the first heavy episode the salt pool is of little importance and organic leachate will only dilute the surface waters; minimum pH values are therefore ~ 4.3 . The E-horizon water becomes more and more mixed with new precipitation and old groundwater and will contribute to a lesser extent to elevated aluminium and hydrogen ion concentrations in the surface waters. The succeeding events may therefore result in lower aluminium concentrations in stream water.

CONCLUSIONS

This study confirms the importance of water pathways for stream water chemistry.

The acidity and aluminium concentrations of soil water in the upper soil horizons (O/H, E) showed considerable temporal variations after the addition of a neutral salt. Pulses of high ionic strength occur naturally, for example due to the large deposition of seasalts. This implies that the assumption of constant chemical composition of the water in selected soil water classes, as claimed in

the EMMA model, is only a rough first approximation, which may be useful in determining water pathways. As a next step the composition of the endmembers corresponding to the O/H and E horizons must be varied, considering in particular the ionic strength.

The potential of a readily mobilized pool of ions coincides with the conditions where the "Birkes model" [31-33] fails to describe aluminium concentrations in stream water satisfactorily. The model includes the accumulation of chloride and sulphate during dry summer periods and the salt pulse at the beginning of snowmelt. However, our results indicate that it may be necessary to use at least three, possibly four, soil reservoirs in a model to reproduce observed $[Al^{3+}]$ satisfactorily, i.e. the H, E, B/C and deeper horizons (valley bottom). It may be satisfactory to combine the last two and even keep the composition constant for short-term models.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge support from the Surface Water Acidification programme (SWAP) and the Norwegian Ministry of Environment. Valuable criticisms were received from C. Neal and J. Mulder.

REFERENCES

- 1 C.S. Cronan and C.L. Schofield, Aluminum leaching response to acid precipitation: effects on high-elevation watersheds in the northeast US, *Science*, 204 (1979) 304-306.
- 2 W. Dickson, Properties of acidified waters, in D. Drablos and A. Tollan (Eds), *Ecological Impact of Acid precipitation*, SNSF, Norwegian Institute for Water Research, Oslo, Norway, 1980, pp. 75-83.
- 3 L.N. Overrein, H.M. Seip and A. Tollan, Acid precipitation — effects on forest and fish, final Report SNSF Project, Norwegian Institute for Water Research, Oslo, Norway, 1980, 175 pp.
- 4 J.O. Reuss and D.W. Johnson, Acid Deposition and the Acidification of Soil and Waters, *Ecological Studies* 59, Springer-Verlag, Berlin, 1986, 129 pp.
- 5 N. Christophersen, H.M. Seip, C. Qvenild and O. Tollan, Sodium mobility in a mini-catchment studied with radioactive tracers and artificial precipitation, *Nord. Hydrol.*, 13 (1982) 105-114.
- 6 R.F. Wright, S.A. Norton, D.F. Brakke and T. Frogner, Experimental verification of episodic acidification of freshwaters by seasalts, *Nature*, 334 (1988) 422-424.
- 7 T.J. Sullivan, N. Christophersen, I.P. Muniz, H.M. Seip and P.D. Sullivan, Aqueous aluminium chemistry response to episodic increases in discharge, *Nature*, 323 (1986) 324-327.
- 8 T.J. Sullivan, N. Christophersen, R.P. Hooper, H.M. Seip, I.P. Muniz, P.D. Sullivan and R.D. Vogt, Episodic variation in streamwater chemistry at Birkes southernmost Norway: Evidence for importance of flow pathways, in *proc. Acidification and Water Pathways*, Norwegian National Committee for Hydrology, Box 5091, Majorstua 0301, Oslo 3, Norway, Vol. I, 1987, pp. 269-279.
- 9 C.S. Cronan, W.J. Walker and P.R. Bloom, Predicting aqueous aluminium concentrations in natural waters, *Nature*, 324 (1986) 140-143.
- 10 C. Neal, Aluminium solubility relationships in acid waters — A practical example of the need for a radical reappraisal, *J. Hydrol.*, 104 (1988) 141-159.
- 11 H.M. Seip, D.O. Andersen, N. Christophersen, T. Sullivan and R.D. Vogt, Variations in concentrations of aqueous aluminium and other chemical species during hydrological episodes at Birkes, southernmost Norway, *J. Hydrol.*, 108 (1989) 387-405.

- 12 I.T. Rosenqvist, Alternative sources for acidification of river water in Norway, *Sci. Total Environ.*, 10 (1978) 39–49.
- 13 J. Nordø, A statistical study of the acidity in a stream near Birkenes in Aust-Agder, in I.T. Rosenqvist (Ed.), *Sur Jord-Surt Vann (Acid soil-acid water)*, Ingeniørforlaget, Oslo, 1977.
- 14 I.M. Cozzarelli, J.S. Herman and R.A. Parnell, The mobilization of aluminium in a natural soil system — Effects of hydrological pathways, *Water Resour. Res.*, 23 (1987) 859–874.
- 15 G.B. Lawrence, C.T. Driscoll and R.D. Fuller, Hydrological control of aluminium chemistry in an acidic headwater stream, *Water Resour. Res.*, 24 (1988) 659–669.
- 16 N. Christophersen, C. Neal, R.P. Hooper, R. Vogt and S. Andersen, Modelling streamwater chemistry as a mixture of soil water endmembers — A step towards second generation acidification models, *J. Hydrol.*, in press.
- 17 J. Mulder, N. Christophersen, M. Hauhs, R.D. Vogt, S. Andersen and D.O. Andersen, Hydrochemical controls in the Birkenes catchment as inferred from a rainstorm high in seasalts, *Water Resour. Res.*, in press.
- 18 F.H. Brække, Hydrochemistry in low-pH-soils of South Norway. 1. Peat and soil water quality, *Medd. Nor. Inst. Skogforskning*, 36 (1981) 11.
- 19 R.B. Barnes, The determination of specific forms of aluminium in natural water, *Chem. Geol.*, 15 (1975) 177–191.
- 20 C.T. Driscoll, A procedure for the fractionation of aqueous aluminium in dilute acidic waters, *Int. J. Environ. Anal. Chem.*, 16 (1984) 267–283.
- 21 W.D. Schecher and C.T. Driscoll, An evaluation of uncertainties associated with aluminium equilibrium calculations, *Water Resour. Res.*, 23 (1987) 525–534.
- 22 T.J. Sullivan, H.M. Seip and I.P. Muniz, A comparison of frequently used methods of the determination of aqueous aluminium, *Int. J. Environ. Anal. Chem.*, 26 (1986) 61–75.
- 23 O.C. Magistad, The aluminium content of the soil solution and its relation to soil reaction and plant growth, *Soil Sci.*, 20 (1925) 181–225.
- 24 H.M. May, P.A. Helmke and M.L. Jackson, Gibbsite solubility and thermodynamic properties of hydroxyaluminum in aqueous solutions at 25°C, *Geochim. Cosmochim. Acta*, 43 (1979) 861–868.
- 25 J.O. Reuss, N. Christophersen and H.M. Seip, A critique of models for freshwater and soil acidification, *Water, Air Soil Pollut.*, 30 (1986) 909–930.
- 26 P.R. Bloom, M.B. McBride and R.M. Weaver, Aluminium organic matter in acid soils: Buffering and solution aluminium activity, *Soil Sci. Soc. Am., J.*, 43 (1979) 488–493.
- 27 SFT, The Norwegian monitoring programme for long-range transported air pollutants. Results 1980–1984. The Norwegian State Pollution Control Authority (SFT), Oslo, Norway, 1986.
- 28 T.J. Sullivan, N. Christophersen and I.P. Muniz, Soil and streamwater chemistry during snowmelt at the Birkenes catchment, Rep. 850701-1, Center for Industrial Research, Oslo, Norway, 1987, 28 pp.
- 29 J. Frank, Soil survey at Birkenes, a small catchment in Aust-Agder county, southern Norway, SNSF Project, TN 60/80, Norwegian Institute for Water Research, 1980, 41 pp.
- 30 S. Andersen, Flowpaths and control of dissolved aluminium in the Birkenes catchment, Aust-Agder county in Southernmost Norway, Thesis, University of Oslo, Norway, 1989, 116 pp. (in Norwegian).
- 31 N. Christophersen, H.M. Seip and R.F. Wright, A model for streamwater chemistry at Birkenes, Norway, *Water Resour. Res.*, 18 (1982) 977–996.
- 32 A. Stone and H.M. Seip, Mathematical Models and their role in understanding water acidification: An evaluation using the Birkenes Model as an example, *Ambio*, 18 (1989) 192–199.
- 33 A. Stone and H.M. Seip, Are mathematical models useful for understanding water acidification? *Sci. Total Environ.* 96 (1990) 159–174.
- 34 A. Skartveit, Relationships between precipitation chemistry, hydrology, and runoff acidity, *Nord. Hydrol.*, 12 (1981) 65–80.
- 35 M. Johannessen and A. Henriksen, Chemistry of snow meltwater. Changes in concentration during melting, *Water Resour. Res.*, 14 (1978) 615–619.

- 36 J.D. Joslin, P.A. Mays, M.H. Wolfe, J.M. Kelly, R.W. Garber and P.F. Brewer, Chemistry of tension lysimeter water and lateral flow in spruce and hardwood stands, *J. Environ. Qual.*, 16 (1987) 152-160.
- 37 C.T. Driscoll, N. van Breemen and J. Mulder, Aluminum chemistry in a forested Spodosol, *Soil Sci. Soc. Am., J.*, 49 (1985) 437-444.
- 38 SFT, The Norwegian monitoring programme for long-range transported air pollutants, *Annu. Rep. 1987*, The Norwegian State Pollution Control Authority (SFT), Oslo, Norway, 1988, TA-629, 200 pp.
- 39 R.D. Vogt, D.O. Andersen, S. Andersen, N. Christophersen and J. Mulder, Streamwater, soil water chemistry, and water flow paths at Birkenes during a dry-wet hydrological cycle, *Surface Water Acidification Programme (SWAP), Final Conf.*, London, 1990.

ARE MATHEMATICAL MODELS USEFUL FOR UNDERSTANDING WATER ACIDIFICATION?

ALEX STONE and HANS M. SEIP

Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, 0315 Oslo 3 (Norway)

ABSTRACT

Computer models play an integral part in the effort to understand the complicated processes which affect ecosystems subjected to acid precipitation. Current research work using the Birkenes model attempts to improve the evaluation of the present model structure and subjects the program to a stringent verification process. Simulation results for years which are not included in, and vary considerably from, the calibration period are described. The importance of model validation is emphasized. The simulations, though in general in fair agreement with the observations, are still deficient in some respects and possible model improvements are discussed. In addition, problems which appeared during model validation are also found during verification procedures. However, computer simulations have provided the chemist with a powerful tool for evaluating current thinking regarding chemical processes involved in environmental problems such as acid precipitation.

INTRODUCTION

Mathematical models used by most researchers are generally constructed either for the testing of hypotheses or for making predictions by altering current conditions. Models for surface water acidification are no exception. In this paper, we will discuss the development, calibration and verification of the "Birkenes model" (BIM), a model constructed as a step towards understanding the complicated effects of acid precipitation upon a vulnerable catchment. We believe that the general approaches used in the evaluation of the BIM are informative and that many of the conclusions apply to other acidification models, regardless of their intent and purpose.

Initial chemical modelling of the Birkenes catchment began in the late 1970s [1,2]. In the original work, important aspects of streamwater chemistry were reproduced, for instance $[H^+]$ was positively and $[Ca^{2+} + Mg^{2+}]$ was negatively correlated with flow. In addition, mineralization of sulphur compounds was found to be necessary to explain the large increase in sulphate concentrations observed after long dry periods, and it was also shown that the *amount*, but not the *chemistry*, of the precipitation causing the event, is critically important for the streamwater chemistry, as pointed out earlier by Rosenqvist [3]. This work confirmed the importance of mobile anions [4].

THE BIRKENES CATCHMENT; FIELD STUDIES

The work described in this paper uses data from the Birkenes catchment, which encompasses an area of 0.41 km² and is located in southern-most Norway. The average pH of precipitation is about 4.2 and sulphur deposition is approximately 2 g S m⁻² year⁻¹ [5]. The catchment has shallow podzolic soils on granitic bedrock, is covered by natural spruce forest and is drained by a third-order stream. Hydrological and chemical measurements have been made at the Birkenes catchment since 1971. The Norwegian Institute for Water Research (NIVA) is responsible for streamwater data and the Norwegian Institute for Air Research (NILU) for precipitation and air sampling. Intensive studies during hydrological events, such as snowmelt and heavy autumnal rainstorms, have been conducted since 1984 [6].

Major anions and cations are determined by ion chromatography and atomic absorption spectroscopy, respectively. Aluminium species are fractionated as described by Sullivan et al. [7]. Concentrations of fluoride, necessary for calculating the concentrations of Al³⁺, are not determined in the routine analyses carried out by NIVA. A total aluminium fluoride concentration in streamwater of 5 μ M was assumed, based on values determined during episodic studies [6].

THE BIRKENES MODEL

The Birkenes model takes its name from the Birkenes catchment. However, modified versions have been applied in several others [8,9]. The basic structure of the model is given in Fig. 1 and the key processes involved are described in the Appendix. The hydrological model has not been greatly altered since its conception [10]. It consists of two compartments, with the upper (A) representing a mostly organic soil horizon providing quick flow, and the lower (B) deeper soil layers providing base flow. A snow reservoir is included when needed. Water may be routed from the upper compartment directly to the stream or to the lower compartment. The current versions include the possibility of "piston flow", which allows water from A to flush out an equivalent amount of water from B, thereby altering the chemical quality but not the quantity of water entering the stream [11].

The mobile anion concept [4] is a key feature of the model. The relative concentrations of cations in the water in the upper reservoir are determined by exchange reactions (Appendix). The relationship

$$[Al^{3+}] [H^+]^{-3} = K_{Al} \quad (1)$$

is assumed to be valid in both soil reservoirs. This may be thought of as equilibrium with some types of Al(OH)₃ (gibbsite) or as simple ion exchange, depending on the value of K_{Al} . For further model details see Appendix and Rustad et al. [8].

An optimization procedure, which minimizes an objective function (the weighted sum of squares of the differences between observed and predicted

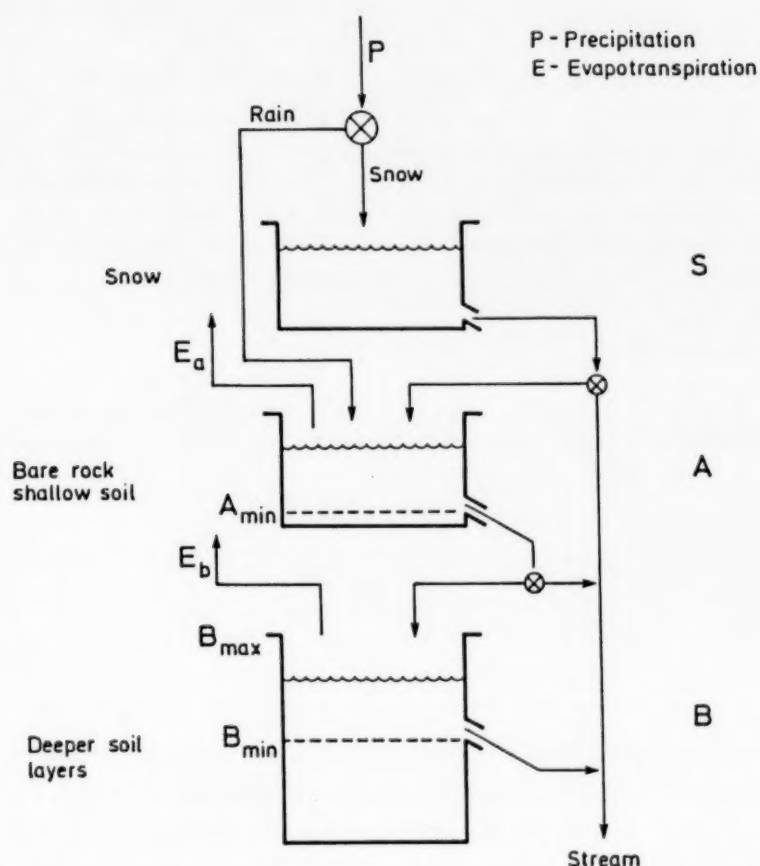


Fig. 1. The Birkenes model.

values), has recently been added to the model [12,13]. This routine makes it possible to optimize model parameters in both the hydrological and chemical sub-models either separately or simultaneously.

EARLIER WORK ON MODEL EVALUATION

The work presented here is a continuation of work published by Stone and Seip [14] and earlier work by Hooper et al. [13]. The basic points of interest concern the need for model validation through the use of conservative tracers and extended simulation periods. The BIM was subjected to an in-depth parameter analysis for both the hydrological and chemical sub-models. The program was extended to allow simulation and optimization of long data records (3.5 years). High data quality and long periods increase the ability of the optimization procedure to determine parameter values for the existing model structures. Two species were used as conservative tracers, the heavy isotope of oxygen bound in water ($H_2^{18}O$, subsequently referred to as ^{18}O) and the Cl^- ion. It is possible to consider the Cl^- ion as an approximation of a conservative tracer in the Birkenes catchment because of the high seasalt input and because there exists no significant source of chloride within the catchment. This assumption may not be valid for other catchments which do not possess the same physical characteristics, and other researchers should be careful to check

TABLE 1

Results of hydrological parameter definition from an optimization run where discharge, ^{18}O and Cl^- observations were used simultaneously. The various parameters are defined as follows (cf. Fig. 1): minimum water level in B above which discharge is allowed (B_{\min}); size of Reservoir B (B_{size}) — this parameter is defined in the model as the difference in the lower reservoir (B) between the maximum level and minimum level of water giving discharge; minimum water level in A above which discharge is allowed (A_{\min}); daily discharge as percentage of water in Reservoir A (Q_A); daily discharge as percentage of water in Reservoir B (Q_B); limit for routing of flow from A to B (A_{ksmx}) and piston flow factor (P_{FACT}).

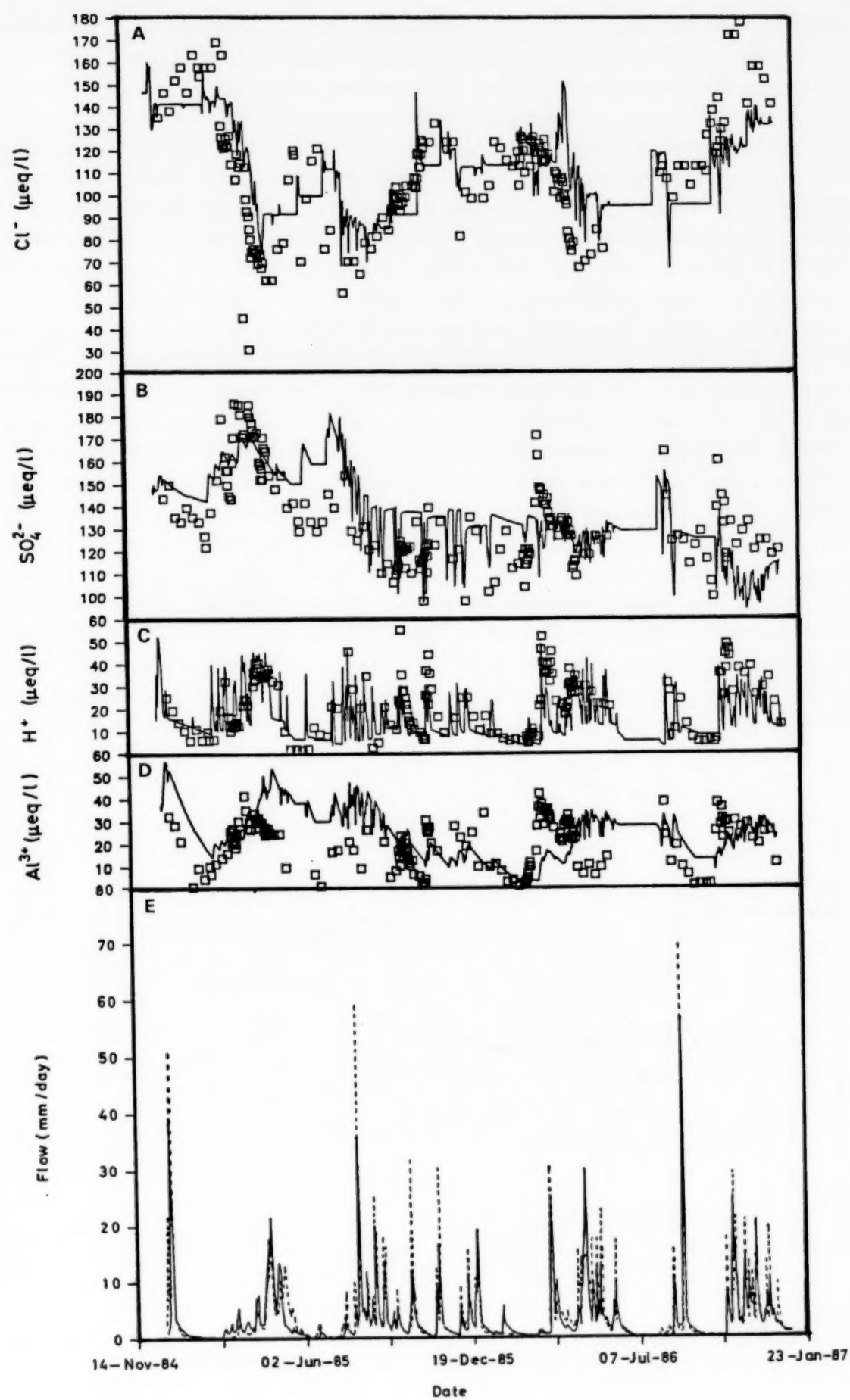
	Flow, ^{18}O and Cl^- (piston flow included)
B_{\min} (mm)	175.4
B_{size} (mm)	32.8
A_{\min} (mm)	33.3
Q_A (day^{-1})	1.78
Q_B (day^{-1})	0.09
A_{ksmx}	0.35
P_{FACT}	0.37

whether it is valid for their catchments before performing similar analyses.

The results of the simulations (Fig. 2) using parameter values (Table 1) determined by Stone and Seip [14] show that the model produces a good representation of discharge, ^{18}O and Cl^- . The discharge (Fig. 2E) is under-predicted during many of the periods of high flow and problems still exist for the two tracers during snowmelt periods. However, the simulation follows the main trends and provides adequate agreement with observed data.

The chemical portion of the BIM was then subjected to detailed evaluation, with particular emphasis placed upon three species, Al^{3+} , SO_4^{2-} and H^+ . The results of these analyses showed that, although the model reproduces the overall trends fairly well, there still exist areas which require further improvement. In addition, it was suggested that the Al^{3+} – H^+ relationship used [Eqn (1)] does not adequately represent the aluminium processes occurring in the Birkenes catchment. This is in agreement with soil sample studies conducted within our group [15], which indicated that $[\text{Al}^{3+}]$ does not increase with $[\text{H}^+]^3$ as suggested by Eqn (1), but rather that the exponent may be in the range 1.7–2.6. The simulation of the H^+ concentrations is quite representative (Fig. 2C), with both baseline values and peak values adequately met. The same cannot be said for the Al^{3+} species, which experience insufficient variation and

Fig. 2. Simulated and observed concentrations for various anionic and cationic species in stream-water and for discharge within the Birkenes catchment. The period shown extends from 1 January 1985 to 31 December 1986, but is taken from a simulated period from 1 June 1983 to 31 December 1986. All simulations use optimized parameters and include piston flow. (A) Simulated (—) and observed (\square) Cl^- concentrations. Cl^- is considered as a conservative tracer. (B) Simulated (—) and observed (\square) SO_4^{2-} concentrations. (C) Simulated (—) and observed (\square) H^+ concentrations. (D) Simulated (—) and observed (\square) Al^{3+} concentrations. (E) Simulated (—) and observed (---) discharge.



poor baseline determination. A possible reason for this deviation is that, in the current version of the BIM, precipitation on, and redissolution from, the stream bed are not correctly included. The concentration of Al^{3+} is determined only by mixing of the two incoming concentrations and no gibbsite relationship is forced. It has been suggested that aluminium hydroxide may precipitate in the stream. This may occur, for example, during periods with high aluminium concentrations or during periods when the pH is altered by the degassing of CO_2 . The aluminium could then later redissolve during periods of low concentrations or high acidity [16]. A further possibility is that a combination of processes, some of which may yet be unidentified, may in fact be the naturally occurring mechanism. The most obvious and important conclusions to be gained from this work concern the validity of the Al^{3+} sub-model.

The simulation of the remaining cations (Na^+ , Ca^{2+} and Mg^{2+}) reproduced well the observed stream concentrations. Na^+ was also treated as a conservative tracer in the upper reservoir, but weathering was allowed in the deeper soil layers (Reservoir B). During periods of high seasalt input, sodium also participates in ion exchange in Reservoir A [17]. Considering the quality of the simulation, this model was not altered to include ion exchange, but future improvements in this direction should be considered.

A comparison was made between the results obtained by Stone and Seip [14] using extended data sets and results reported by Hooper et al. [13], who calibrated the model using observations only from snow-free seasons. The 1983 season was selected as representative of the results obtained for short calibration periods (on the order of 200 days). Figure 3 shows the comparison of two

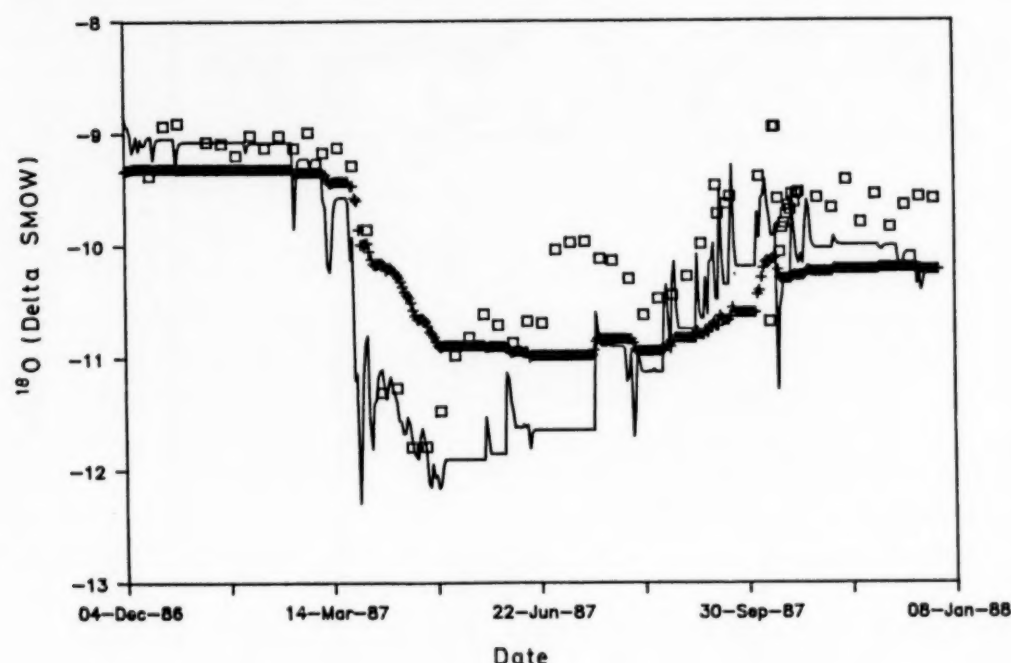


Fig. 3. ^{18}O values for the non-optimized year 1987 using parameter values (Table 1) from Stone and Seip [14] (—), from results reported by Hooper et al. [13] (+), and for observed stream concentrations (\square).

simulations for ^{18}O using the 1987 data. The results demonstrate that the values reported using a very short calibration period, although adequate for that period, give less satisfactory results for other years. This is particularly important for the chemical sub-models where the overly dampened signal restricts chemical variability in the cationic and anionic simulations. The use of extended data sets allows a better determination of parameter values for the various processes within a catchment, thereby increasing their validity. In addition, it demonstrates that the results of a model prediction are only as good as the quality of the parameter values used. Simulation models which are used for predictive purposes must undergo stringent parameter evaluation if the predictions obtained are to be accepted as valid and truly representative of changes in natural processes and conditions.

CURRENT WORK

An area of great importance not addressed by our earlier work was the verification of the parameter values using data for periods other than those used in the calibration procedure. If the parameter values determined in previous work [14] for the hydrological and chemical sub-models represent a reasonable approximation of current soil processes, the same parameter values should produce adequate simulations for other periods. With this objective in mind, the years 1987 and 1976 were chosen for verification. These years were meteorologically quite different. 1987 was a very wet year containing few periods with no discharge from the catchment. The database is good, including measurements of ^{18}O and aluminium speciation. 1976 was selected mainly because the spring and summer of that year were extremely dry, offering the possibility of evaluating the ability of the model to simulation discharge and chemical species after long dry spells.

For both years, the simulations were begun during the early summer of the previous year and allowed to continue through the year of interest. The lack of data for snow parameters such as depth of snow pack made it impossible to start the simulation in the middle of winter. The results reported (Figs 4 and 5) are those for the period from January 1 to December 31. The data from the previous summer and autumn are not shown. Observations of ^{18}O and the concentrations of Na^+ and Cl^- in precipitation were not available for 1976. The values for the ionic species were calculated using the concentration of Mg^{2+} and the relative concentrations of Na^+ and Cl^- in seawater. These values undoubtedly vary slightly from the true values but are, however, the best approximation which can be made from existing data. The ability of the model to simulate these species, therefore, can be best evaluated from the simulation for 1987.

Another problem which had to be addressed concerned parameter initialization. In the current simulation procedure, most initial stores of cations and anions present are obtained from the first available observed concentrations in the stream. The only exceptions are $[\text{Al}^{3+}]$, $[\text{HCO}_3^-]$ and $[\text{Ca}^{2+}]$. The Al^{3+} and HCO_3^- concentrations are determined from equilibrium relationships with the

observed H^+ concentration and the appropriate equilibrium constants. The Ca^{2+} concentration is then calculated so that the ionic balance is maintained. If the first observed H^+ concentration is very high, it will produce a high Al^{3+} concentration and, potentially, a negative value for Ca^{2+} . At present we solve this problem by choosing the starting point carefully but, in this respect, the program needs to be improved.

Hydrological and conservative tracer simulations

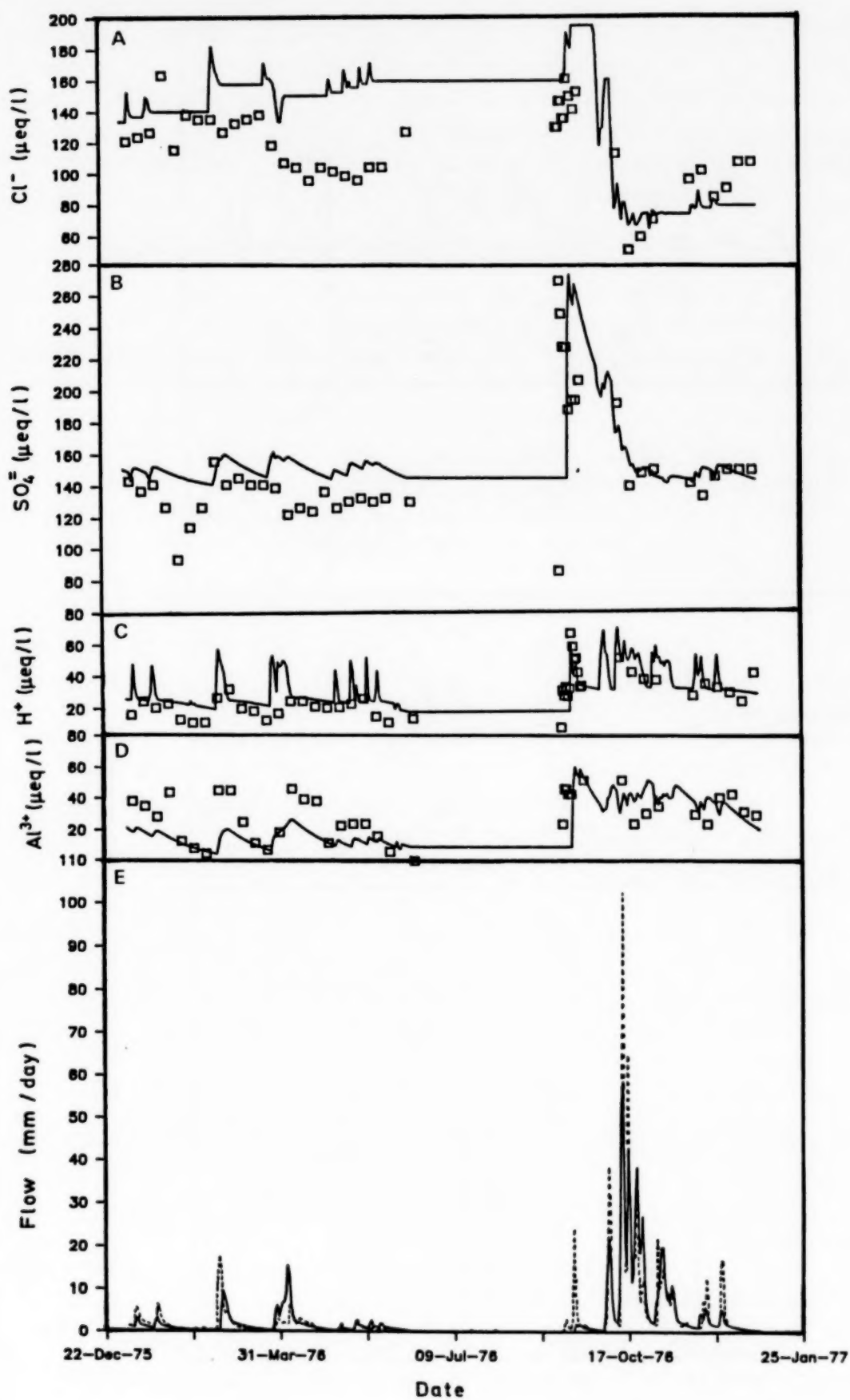
The results for discharge for 1976 and 1987 are shown in Figs 4E and 5E, respectively. As was the case in earlier work, the discharge tends to be underestimated by the current hydrological model for both years. There exist a couple of other points where the simulations are lacking. The peaks following the extended dry period in 1976 are seriously under-estimated. With the present model structure, the BIM requires both reservoirs to be filled to their minimum values after dry periods before substantial flow to the stream can be realized. This sometimes leads to serious under-estimation of peaks immediately following dry spells.

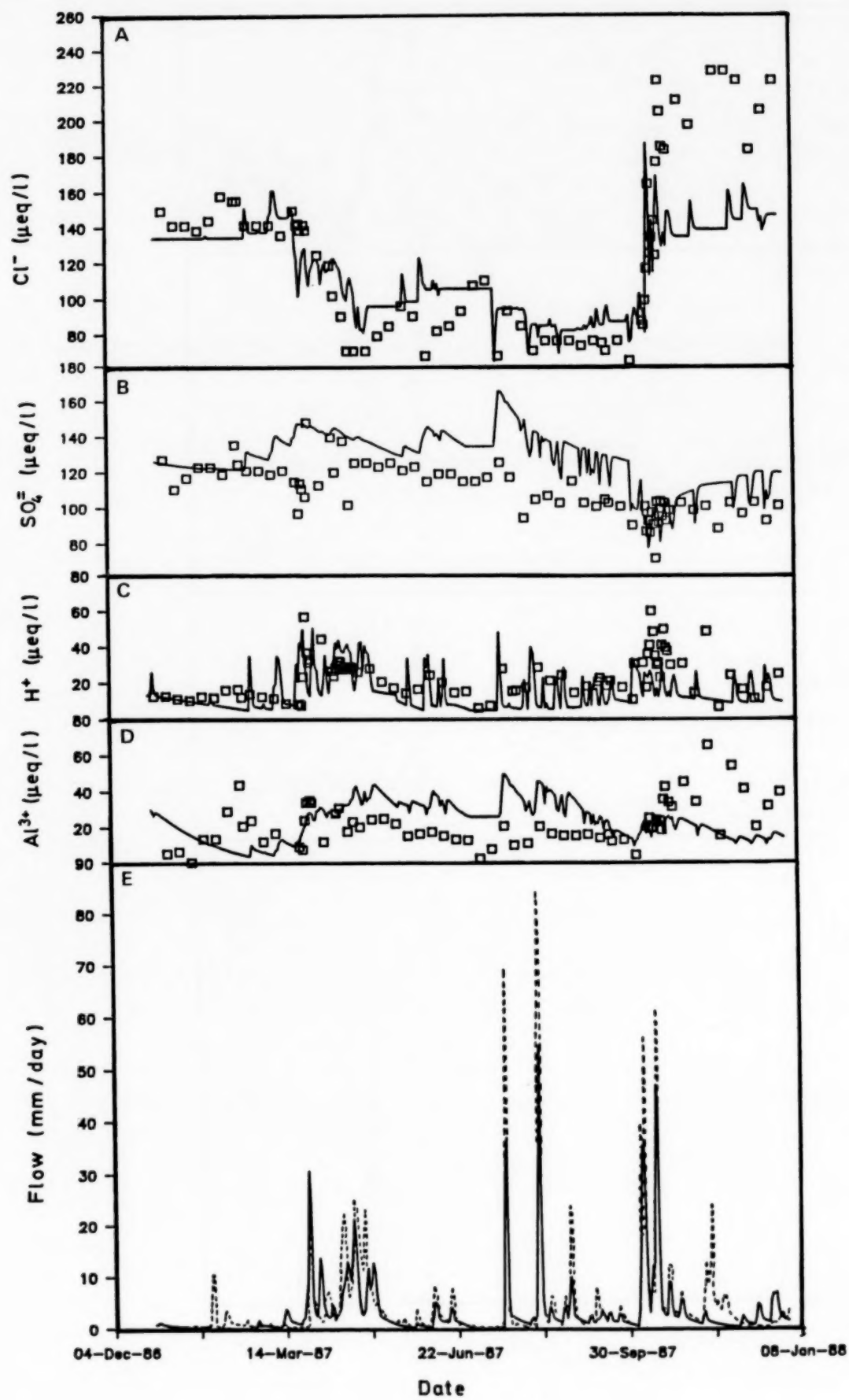
The peaks in the autumn of 1987 are also low, which is caused by a feature of the current snow routine. During periods with daily average temperatures below freezing, the model assumes all precipitation occurs and remains as snow. The model is, therefore, very sensitive to small variations in temperature around $0^{\circ}C$. Soil warmth may also melt considerable amounts of snow, generating flow from the catchment, a process which is not adequately represented by the present structure. These deficiencies in discharge, although not large, may cause problems in the chemical simulations.

The Cl^- and Na^+ for 1987 are well reproduced by the current structure. The Cl^- simulation (Fig. 5A) is lacking only in the autumn of 1987, which is most probably due to the flow problems mentioned earlier. No equivalent problem is observed in the Na^+ simulation, which reflects stream concentrations very closely. The simulation of Cl^- for 1976 (Fig. 4A) produces an adequate simulation given the data restraints mentioned earlier. There exists a tendency for the Cl^- level to increase with time. This may be due to variability in chloride dry deposition during years with an extensive dry period. The current model may over-predict the dry deposition during this period. The agreement improves during the autumn, when more discharge from the catchment is observed.

Overall, the discharge is well reproduced for both verification years and,

Fig. 4. Simulated and observed concentrations for various anionic and cationic species in stream-water and for discharge within the Birkenes catchment. The period shown extends from 1 January 1976 to 31 December 1976, but is taken from a simulated period from 1 June 1975 to 31 December 1976. (A) Simulated (—) and observed (\square) Cl^- concentrations. Cl^- is considered as a conservative tracer. (B) Simulated (—) and observed (\square) SO_4^{2-} concentrations. (C) Simulated (—) and observed (\square) H^+ concentrations. (D) Simulated (—) and observed (\square) Al^{3+} concentrations. (E) Simulated (—) and observed (---) discharge.





disregarding certain deficiencies which also exist in the calibration period, the BIM reproduces stream concentrations within the limitations expected with the present model structure.

Chemical simulations

The chemical simulations were then analyzed in detail. The results of the simulations for SO_4^{2-} , H^+ and Al^{3+} are shown in Figs 4(B-D) and 5(B-D) for 1976 and 1987, respectively. The simulation of SO_4^{2-} (Fig. 4B) during the dry year of 1976 is good with most of the general trends well reproduced by the model. The observed values show slightly more variation in concentration and there exists a slight tendency to over-predict the baseline concentrations during the dry period; however, the large increases after the two dry periods (one of which was in 1975 and is not shown in Fig. 4B) are well represented, providing verification that the model works adequately during dry years. The sulphate simulation for 1987 shows that wet years are equally well reproduced. The model generally over-predicts the baseline concentrations during the summer and autumn and gives smaller fluctuations during the spring and summer periods than are found in the observed stream values. This may indicate that the mineralization and reduction processes may experience greater variability during wet periods than are demonstrated in the current model structure. The model does, however, provide an adequate simulation.

The simulations for Al^{3+} and H^+ are also slightly different for these two years. The H^+ concentrations are well reproduced for 1987, both with respect to baseline concentrations and short-term variations. The largest deficiency is during the autumn of 1987 and is probably due to problems within the discharge simulation and not the H^+ sub-model itself. The results for 1976 are also good. The general trends and levels are well reproduced, although a higher baseline concentration is simulated than is observed. A slight over-estimation of the baseline values in the SO_4^{2-} simulation could affect the H^+ simulation. In addition the soil may have acidified slightly from 1976 to 1983, implying that the ion exchange constants could have been different for the two years.

The results for the Al^{3+} simulation are more divergent. For 1987, the model fails to reach observed stream concentrations during two portions of the snow periods. The first is during the beginning of snowmelt and the second is during late autumn. In both instances the snow routine fails to simulate observed discharge adequately, which then adversely affects chemical simulations. This is an example of how deficiencies in hydrology can propagate throughout a

Fig. 5. Simulated and observed concentrations for various anionic and cationic species in stream-water and for discharge within the Birkenes catchment. The period shown extends from 1 January 1987 to 31 December 1987, but is taken from a simulated period from 1 June 1986 to 31 December 1987. (A) Simulated (—) and observed (□) Cl^- concentrations. Cl^- is considered as a conservative tracer. (B) Simulated (—) and observed (□) SO_4^{2-} concentrations. (C) simulated (—) and observed (□) H^+ concentrations. (D) Simulated (—) and observed (□) Al^{3+} concentrations. (E) Simulated (—) and observed (---) discharge.

simulation. If, however, these factors are removed from consideration, the general trend of the simulation is to over-predict observed concentrations. This may reflect a relationship other than that demonstrated with Eqn (1). Similar disagreements were found for the calibration period.

The results for 1976 are in contrast to those obtained previously. In this instance, the simulated values produce good baseline values, but the responses are dampened compared with those observed in the stream. Good agreement is obtained only during the autumn period. Thus under-estimation can occur for a variety of reasons, the most probable being the quality of Al^{3+} data available. In 1976, the Al values observed in the stream are for the total aluminium, including colloidal and complexed forms. The Al^{3+} concentration was obtained by subtracting $26 \mu\text{eq l}^{-1}$ for both the fluoride and organically complexed aluminium. This average value may not be appropriate in all periods, in particular, three values after the long dry period which were in the order of $200 \mu\text{eq l}^{-1}$ seemed abnormally high and are removed from Fig. 4D to save space. For the other years, labile Al concentrations corresponding closely to inorganic Al species were determined and $[\text{Al}^{3+}]$ estimated by subtracting $15 \mu\text{eq l}^{-1}$ for the fluoride complexes. These values are more representative of the aluminium species causing biological damage [18].

The simulations for the remaining species (Ca^{2+} and Mg^{2+}) are well reproduced during both verification years. The general processes affecting these species appear to be well represented by the current model structure.

As mentioned earlier, laboratory results from our group indicate that Eqn (1) does not hold [15]. To obtain a model in better agreement with the soil studies, we changed the relationship in Eqn (1) to:

$$[\text{Al}^{3+}] [\text{H}^+]^{-2} = K_{\text{Al}} \quad (2)$$

in the upper reservoir. The original relationship was retained for the lower reservoir. To maintain the ion balance, the BIM adjusts the Ca^{2+} concentrations. This is considered sufficiently satisfactory to obtain an estimation of the effect of changing from Eqn (1) to Eqn (2), although it would probably be more realistic to adjust the SO_4^{2-} concentrations. The model was then optimized as described earlier [13,14]. The changes resulted in slight improvements in the aluminium and few alterations in the H^+ simulations, but the agreement is still not satisfactory. Further model development seems warranted.

In general, the model parameters determined in previous model work [14] produce equivalent simulations for years not included in the calibration procedure. The model deficiencies which were determined earlier still exist, thereby indicating areas for future research and improvement. However, those species which are well reproduced for the calibration period with the current structure and optimized parameter values are also well reproduced for verification years. This provides support for the concept that the optimization and model validation procedure is a useful tool for evaluating currently existing acidification models.

CONCLUSIONS

The current work demonstrates that it is important to subject a model to extensive parameter evaluation and validation. Parameter values obtained using different, short calibration periods possessed considerable variability and produced simulations which varied significantly from each other. Our work supports the premise that the longer the calibration period and the more data used, the better the quality of the parameter values obtained. In addition, it is important to use independent verification periods reflecting different meteorological conditions. We found that it is possible to obtain parameter values consistent with many observed data for many years. These parameters give predictions of similar quality during verification years as for the calibration periods.

As a general summary, it is possible to draw certain conclusions from the results presented above and other modelling work not discussed in detail here.

— *Models have proved very useful for testing hypotheses.* It is easy to formulate qualitative models. Quantification of the model processes is necessary for evaluating these hypotheses.

— *Improvements are needed.* Despite the general agreement between observed and simulated values, we believe that several sub-models can be improved. Modifications in sub-models for hydrological routing and aluminium, for example, seem most crucial. For long-term predictions, the sulphur model needs improvement.

— *Modelling work has given important feedback to field studies.* Our modelling experience was particularly important in planning studies of ^{18}O isotope concentrations and studies using soil lysimeters, piezometers and tensiometers. New observations have given the basis for further model development.

— *Model predictions are still tentative.* The value of the predictions obtained from any model is only as good as the model and parameter values upon which it is based. The more stringent the validation and analysis of the model and its contents, the better the prediction.

— *More emphasis must be put on model validation.* Several types of studies are useful in this respect, such as detailed studies in natural catchments, manipulation experiments with precipitation of varying chemistry and studies around point sources with changing emissions.

— *One must check model parameters against data sets not used in the calibration process.* In this way, it can be seen whether the processes included in the model are, at least to some degree, representative of those which occur in nature. The less the conditions differ from those used for calibration, the more assurance can be placed upon a model's ability to simulate nature.

— *One can learn as much from the failure of a model simulation as from its success.* The assessment of errors and the postulation of reasons for their existence are necessary to evaluate the processes used and to obtain ideas for model improvements.

Reservoir A (upper soil horizons)

Rain and meltwater with appropriate concentrations of ions enter as input. Dry deposition of S, Cl, and Na is added to this reservoir during the snow-free season, otherwise dry deposition is added to the snowpack.

The main equations determining the concentrations in discharge from A are: The charge balance:

$$[\text{H}^+] + [\text{Na}^+] + [\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{Al}^{3+}] = [\text{SO}_4^{2-}] + [\text{Cl}^-] + [\text{HCO}_3^-] \quad (\text{A1})$$

Equations determining cation concentrations:

$$K_{\text{Al}} = [\text{Al}^{3+}]/[\text{H}^+]^3 \quad (\text{A2})$$

$$K_{\text{Ca}} = [\text{Ca}^{2+}]^3/[\text{Al}^{3+}]^2 \quad (\text{A3})$$

$$K_{\text{Mg}} = [\text{Mg}^{2+}]/[\text{Ca}^{2+}] \quad (\text{A4})$$

$[\text{Na}^+]$ is assumed not to be affected by chemical processes in this reservoir, i.e. it is a conservative tracer.

Equations determining anion concentrations:

$$[\text{HCO}_3^-] = KP_{\text{CO}_2}/[\text{H}^+] \quad (\text{A5})$$

P_{CO_2} is the CO_2 pressure which is assigned a fixed value of 10 times atmospheric P_{CO_2} .

$$[\text{SO}_4^{2-}] = F_A/(K_A + W_A) \quad (\text{A6})$$

F_A is the amount of water-soluble sulphate both in the solution and solid phases, W_A the water level and K_A a constant.

Mineralization adds sulphate to F_A during dry periods and when there is a thick snowpack

$$S_{\text{miner A}} = K_{\text{min A}} (A_{\text{min}} - 0.2 \cdot W_A)/A_{\text{min}} \quad (\text{A7})$$

W_A is the water level in Reservoir A and $K_{\text{min A}}$ is a constant mineralization rate. If $W_A > A_{\text{min}}$, $S_{\text{miner A}}$ is set equal to zero. When there is a snowpack with a water equivalent of ≥ 50 mm, mineralization is assumed to occur at double the rate of that in Eqn (A7).

During wet periods, sulphate may be removed from the solution (e.g. by reduction)

$$S_{\text{red A}} = (T_s - 5.0) K_{\text{red A}}/10.0 \text{ (for } 5 < T_s < 15^\circ\text{C)} \quad (\text{A8})$$

T_s is the soil temperature and $K_{\text{red A}}$ the maximum reduction rate. At $T_s > 15^\circ\text{C}$, $S_{\text{red A}} = K_{\text{red A}}$, and at $T_s < 5^\circ\text{C}$, $S_{\text{red A}} = 0$. Cl^- is assumed to be conservative.

Reservoir B (lower soil horizons)

Equations (A1) and (A2) are assumed valid, but the constant K_{A1} in (A2) has different values in the two reservoirs. H^+ ions are consumed by weathering, producing Ca^{2+} , Mg^{2+} and Na^+ ions. The amount of Ca^{2+} , Mg^{2+} and Na^+ obtained is equivalent to the amount of H^+ ion removed in the weathering process, which is calculated by the following equation:

$$H_{wthr}^+ = K_w W_B ([H^+]_B - [H^+]_{E_B}) \quad (A9)$$

H_{wthr}^+ is the amount of H^+ weathering, K_w is a rate constant, W_B is the amount of water, $[H^+]_B$ the $[H^+]$ and $[H^+]_{E_B}$ the equilibrium $[H^+]$ in Reservoir B.

Equation (A5) is used for $[HCO_3^-]$, but with a CO_2 pressure varying with temperature [8]. Cl^- is assumed to be conservative.

The SO_4^{2-} concentration is controlled by two pools of sulphur, one soluble and one fixed. Transfer between these two pools is dependent upon the amount of water in the reservoir and the difference between the current and equilibrium SO_4^{2-} concentrations. A small amount of reduction is included and, unlike in Reservoir A [Eqn (A8)], the amount is solely dependent upon the water level in the reservoir. However, its contribution is small. Otherwise, the concentration is calculated using an equation similar to (A6) with a different value for F_A .

Stream

Equations (A1) and (A5) are assumed to apply. The CO_2 pressure was set at four times the partial pressure of CO_2 in the atmosphere. Equation (A2) is only in force if the product $[Al^{3+}][H^+]^{-3}$ exceeds a given value, in which case $Al(OH)_3$ is assumed to precipitate. In the present work, this constant was set at a high value and no removal of Al^{3+} occurred. The concentrations of Al^{3+} , as well as other cations and anions, were obtained by mixing the discharges from the two reservoirs.

REFERENCES

- 1 N. Christophersen and R.F. Wright, Sulfate budget and a model for sulfate concentration in streamwater at Birkenes, a small forested catchment in southernmost Norway, *Water Resour. Res.*, 17 (1981) 377-189.
- 2 N. Christophersen, H.M. Seip and R.F. Wright, A model for streamwater chemistry at Birkenes, Norway, *Water Resour. Res.*, 18 (1982) 977-996.
- 3 I.Th. Rosenqvist, Alternative sources for acidification of river water in Norway, *Sci. Total Environ.*, 10, (1978) 39-49.
- 4 H.M. Seip, Acidification of freshwater — sources and mechanisms, in D. Drabløs and A. Tollan (Eds), *Ecological Impact of Acid Precipitation*, SNSF Project, 1432 Ås-NLH, Norway, 1980, pp. 358-365.
- 5 The Norwegian Monitoring Programme for Long-Range Transported Air Pollutants, TA-606, Project Report 230/86, The Norwegian State Pollution Control Authority, Box 8100, Dep, 0032 Oslo, Norway, 1986.

- 6 H.M. Seip, D.O. Andersen, N. Christophersen, T.J. Sullivan and R.D. Vogt, Variations in concentrations of aqueous aluminium and other chemical species during hydrological episodes at Birkenes, southernmost Norway, *J. Hydrol.*, 108 (1989) 387-405.
- 7 T.J. Sullivan, H.M. Seip and I.P. Muniz, A comparison of frequently used methods for the determination of aqueous aluminum, *Int. J. Anal. Chem.*, 26 (1986) 61-75.
- 8 S. Rustad, N. Christophersen, H.M. Seip and D. Dillon, Model for streamwater chemistry of a tributary to Harp Lake, Ontario, *Can. J. Fish. Aquat. Sci.*, 43 (1986) 625-633.
- 9 D.C.L. Lam, A.G. Bobba, D.S. Jeffries and D. Craig, Modelling stream chemistry for the Turkey Lakes watershed: comparison with 1981-84 data, *Can. J. Fish. Aquat. Sci.*, 45(Suppl. 1) (1988) 72-80.
- 10 D. Lundquist, Modellering av hydrokjemi i nedbørfelter. (Hydrochemical modelling of drainage basins). SNSF Project, IR31-/77, NISK, 1432 Ås-NLH, Norway, 1977.
- 11 H.M. Seip, R. Seip, P.J. Dillon and E. deGrosbois, Model of sulphate concentration in a small stream in the Harp Lake catchment, Ontario, *Can. J. Fish. Aquat. Sci.*, 42 (1985) 927-937.
- 12 E. deGrosbois, R.P. Hooper and N. Christophersen, A multi-signal automatic calibration methodology for hydrochemical models: A case study of the Birkenes model, *Water Resour. Res.*, 24 (1988) 1299-1307.
- 13 R.P. Hooper, A. Stone, N. Christophersen, E. deGrosbois and H.M. Seip, Assessing the Birkenes model of stream acidification using a multi-signal calibration methodology, *Water Resour. Res.*, 24 (1988) 1308-1316.
- 14 A. Stone and H.M. Seip, Mathematical models and their role in understanding water acidification: An evaluation using the Birkenes model as an example, *Ambio*, 18 (1989) 192-199.
- 15 S. Andersen, Chemistry Department, University of Oslo, Oslo, Norway, personal communication.
- 16 S.A. Norton, A. Henriksen, B.M. Wathne and A. Veidel, Aluminium dynamics in response to experimental additions of acid to a small Norwegian stream, in *Proc. Int. Symp. Acidification and Water Pathways*, Bolkesjø, Norway, May 1987, The Norwegian National Committee for Hydrology, P.O. Box 5091 MAJ, Oslo 3, Norway, 1987. pp. 249-258.
- 17 J. Mulder, N. Christophersen, M. Hauhs, R.D. Vogt, S. Andersen and D.O. Andersen, Hydrochemical controls in the Birkenes catchment as inferred from a rainstorm high in seasalts, *Water Resour. Res.* (in press).
- 18 I.P. Muniz, The effects of acidification on Scandinavian freshwater fish fauna, *Philos. Trans. R. Soc. London*, B305 (1984) 517-528.

ALUMINIUM MOBILIZATION IN SOIL AND STREAM WATERS AT THREE NORWEGIAN CATCHMENTS WITH DIFFERENT ACID DEPOSITION AND SITE CHARACTERISTICS

NILS CHRISTOPHERSEN¹, COLIN NEAL², ROLF VOGT³, JACQUELINE M. ESSER⁴ and SJUR ANDERSEN⁵

¹*Center for Industrial Research, P.O. Box 124 Blindern, 0314 Oslo 3 (Norway)*

²*Institute of Hydrology, Maclean Building, Crowmarsh Gifford, Wallingford OX10 8BB (United Kingdom)*

³*Environmental Analysis Inc., P.O. Box 51, 1315 Nesoya (Norway)*

⁴*Norwegian Forest Research Institute, 1432 Aas-NLH (Norway)*

⁵*Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, 0315 Oslo 3 (Norway)*

ABSTRACT

Streamwater, soil water, and soil chemistry data are collated for three small (18–41 ha) Norwegian headwater catchments and intercomparisons are made to allow assessment of the effects of acid deposition on aluminium mobilization. Two of the sites (Birkenes I and II), situated in the most heavily impacted area of southern Norway, show pronounced differences in streamwater chemistry, especially at highflow. The pH and inorganic monomeric aluminium (Al_i) at Birkenes I reach 4.2 and $20 \mu M$ respectively, compared with pH 5–4.6 and $3 \mu M$ Al_i at Birkenes II. The third catchment (Ingabekken) is in a pristine area in mid-Norway where streamwater pH changes from 7.2 at baseflow to ~ 5 at highflow; in this case, Al_i is generally $< 1 \mu M$. The differences in streamwater chemistry are mirrored in the soil solution composition at the three sites. Major differences also occur in the compositions of exchangeable ions, even though cation exchange capacities are similar. In the pristine area, exchangeable aluminium is low, with the exchange complex being dominated by H^+ ; this contrasts with the impacted sites where exchangeable aluminium is much more predominant, especially at Birkenes I. It is concluded that one of the main changes observed during acidification is the conversion of the soil exchange complex from a hydrogen-dominated form to one where aluminium plays an increasingly important role. Such a transformation is not included in most acidification models and should therefore be a focus for further model development.

INTRODUCTION

Qualitatively, the causal relationship between acid deposition and acidified streamwaters in acid-sensitive, granitic areas is now well established. However, on the quantitative side there are still uncertainties concerning the processes operating, although agreement exists among many workers as to the types of key processes that should be considered. For example, several mathematical models for soil and freshwater acidification, such as ILWAS [1], the Birkenes model [2, 3] and MAGIC [4], are all based on the mobile anion concept and include sulphate adsorption, cation exchange, aluminium hydroxide

(gibbsite) equilibrium, and base cation weathering as major processes [5]. However, these models differ with respect to the mathematical process formulations and it is important to utilize new field data as it becomes available for a continuous reevaluation of acidification models.

In this report, data on soil, soil water, and streamwater are brought together from three Norwegian field studies carried out as part of the joint British-Scandinavian Surface Water Acidification Programme (SWAP). The sites have been chosen so as to allow comparisons over a range of deposition and catchment characteristics. Two of the sites, Birkenes I and II in southernmost Norway, lie in the zone of maximum acidic oxide deposition for Norway, but show pronounced differences, with Birkenes II having the better water quality. The third site, Ingabekken in mid-Norway, is in a pristine area receiving only about 10% of the anthropogenic impact of the southern sites. The results include previously published information, albeit in a new comparative setting, from Birkenes I [6, 7] and Ingabekken [8], whereas the data from Birkenes II are presented here for the first time.

SITE DESCRIPTIONS

Birkenes I and II are located 6 km apart, ~30 km north of Kristiansand, southernmost Norway (Fig. 1). These stations receive an estimated total sulphur deposition (wet plus dry) of $\sim 6 \text{ g SO}_4 \text{ m}^{-2} \text{ year}^{-1}$ [9]. The third site, Ingabekken, lies in mid-Norway at Høylandet, ~35 km northeast of the coastal town of Namsos (Fig. 1). This is a pristine area with a low anthropogenic

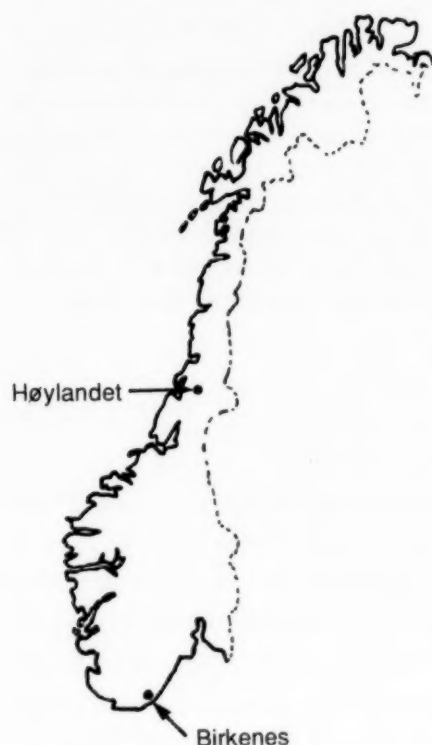


Fig. 1. Location of the study sites in Norway.

TABLE 1

Volume-weighted average precipitation chemistry ($\mu\text{eq l}^{-1}$, except where indicated) at Birkenes I and II for 1986 [9] and for Ingabekken 1986–1987 [8]. "Exc. SO_4 " is sulphate in excess of the seasalt contribution estimated using Cl

	Birkenes I and II	Ingabekken
Water (mm)	1630	1500
pH	4.3	5.0
H^+	54	10
Na	53	90
K	5	4
Ca	9	5
Mg	13	22
NH_4	49	3
NO_3	43	4
SO_4	63	19
Exc. SO_4	56	8
Cl	61	100

impact of $\sim 0.5 \text{ g SO}_4 \text{ m}^{-2} \text{ year}^{-1}$ [10]. Table 1 summarizes precipitation chemistry data.

Ingabekken, the smallest site (18.7 ha), has been studied since 1986 [8]. The catchment lies within the Høylandet study area ($\sim 10 \text{ km}^2$) where several ecological and hydrogeochemical studies are conducted. The bedrock is uniformly granitic, but glacial deposits contain darker amphibole minerals [11]. Høylandet ranges in elevation from ~ 160 to 400 m above sea level with natural Norway spruce stands dominating the lower parts. Ingabekken lies at $\sim 300 \text{ m}$ elevation on the border between the forested and alpine parts and comprises steep, thinly covered hillslopes with peats overlying gleyed soils closer to the brook. No noticeable land-use changes have occurred in recent times. Ingabekken is too small and too inaccessible to support a fish population, but all major streams at Høylandet contain various fish species.

The acidified Birkenes I catchment has been extensively described [2, 6, 7, 12]. Briefly, this spruce-forested catchment (41 ha) on granitic bedrock is mainly covered by thin podzolic and organic soils on steep hillslopes ranging in elevation from ~ 200 to 300 m . Precipitation and streamwater chemistry have been monitored on a routine basis since 1972 with extensive additional episode studies carried out in the spring and autumn since 1984. Major land-use changes have not occurred in recent times. Brown trout spawned in the brook up to about 1950 when a major fish decline occurred; today the streamwater is highly toxic to aquatic biota.

The Birkenes II catchment (30 ha) lies at the same elevation as Birkenes I and comprises two steep subcatchments that merge in a valley where a second-order brook is formed. This brook is disturbed by beaver ponds which have created small marshes along the stream. The bedrock is metamorphosed granite richer in amphibole minerals than Birkenes I. The soils are rather

heterogenous with gleysols and brunisols mixed in with podzols, and the vegetation is dominated by small deciduous trees of various species. Streamwaters have been sampled at several locations at irregular intervals since the autumn of 1985. Land-use changes involved partial planting of one of the upper subcatchments with spruce about 20 years ago, when grazing by domestic animals ceased. The stream enters a bay which still supports one of the very few remaining and sparse brown trout populations in the Birkenes area.

METHODS

The streamwater and soil water data used here were collected during studies conducted in both spring and autumn at the three sites. Soil waters were sampled using tension lysimeters [6, 7]. Birkenes I is well instrumented and soil water data are reported here for 1987 from a total of 17 lysimeters situated along a hillslope [7]; at Birkenes II and Ingabekken, three and six lysimeters, respectively, were installed.

Inorganic monomeric (Al_i) and organic monomeric aluminium (Al_o) were determined following the operationally defined Barnes/Driscoll method [13, 14]. Major cations and anions were determined using atomic absorption and ion chromatography, respectively. Total fluorine was determined by an ion-selective electrode after addition of TISAB buffer. Determination of total

TABLE 2

Volume-weighted streamwater chemistry ($\mu\text{eq l}^{-1}$, except where indicated) for 1986 at Birkenes I [9], at Ingabekken for 1986–1988 [8] and Birkenes II (four sampling stations along main brook). Note that averages for Birkenes II and Ingabekken are biased towards the highflow composition due to over-representation of episode samples

	Birkenes I	Birkenes II	Ingabekken
pH	4.55	5.01	5.10
H^+	28	9.7	8.0
Na	104	78	118
K	5	8	6
Ca	51	56	23
Mg	32	35	34
NH_4	—	—	< 1
NO_3	10	13	3
SO_4	131	85	29
Exc. SO_4	119	77	14
Cl	119	81	152
HCO_3	—	—	3
Al_i (μM)	14	3	< 1
Al_o (μM)	4	4.5	2
F (μM)	5 ^a	2	< 1
Si (μM)	62 ^a	46	—
TOC (mg l^{-1})	4.5	3.5	4.5

^a From Seip et al. [6].

—, Not measured.

organic carbon was performed by measuring UV absorbance at 254 nm calibrated on selected samples using persulphate oxidation and IR spectroscopy of the released CO_2 ($R^2 > 0.92$).

Soil profile descriptions and chemical analyses of composite samples have been carried out by the Norwegian Forest Research Institute (NISK) at Birkenes I and II. The composite sample of each horizon was formed from 75 single samples collected over a 300 m² area to give a representative average. Exchangeable cations were determined by extraction with NH_4NO_3 . For Birkenes I, soil data have also been reported by Mulder et al. [7] and by Frank [15]. The soil analyses at Ingabekken were carried out by the Macaulay Land Use Research Institute (MLURI), Aberdeen, which determined exchangeable cations by NH_4OAc extraction at pH 7. With this method an additional extraction is necessary to determine aluminium separately, and this was carried out using NaCl [11]. For base cations, one obtains approximately the same values using either NH_4NO_3 or NH_4OAc extraction, but the total cation exchange capacity (CEC), including H^+ and Al, will be considerably larger in the latter case, implying a lower base saturation. For exchangeable aluminium, results are often reported using KCl extraction, but comparable results are obtained with both NaCl and NH_4NO_3 [11, 24].

RESULTS AND DISCUSSION

Streamwater chemistry

Volume-weighted concentrations of some major species in streamwater are given in Table 2. Figure 2 gives variations in Al_i and H^+ concentrations for Birkenes I and II and discharge for Birkenes I during the autumn of 1986. At Birkenes I there was a sharp increase in H^+ and Al_i concentrations with the first event after the dry spell in mid-October. The H^+ concentration responded positively with discharge throughout the autumn study, whereas $[\text{Al}_i]$, though remaining high, tended to respond negatively with increased runoff after the initial wetting. These patterns at Birkenes I have been related to the increased contribution of runoff from upper, acidic and organic-rich horizons, lower in aluminium, for events following wet antecedent conditions [6, 12].

Figure 2 also shows the much sparser data from the lowest sampling station at Birkenes II. Assuming the specific discharge at Birkenes I to be representative for this station, the results are sufficient to demonstrate that both H^+ and Al_i levels are significantly lower than at Birkenes I. The H^+ concentration also responded in parallel with the discharge at Birkenes II, but the response for Al_i was less pronounced; this was confirmed by considering all Al_i data for Birkenes II.

At Ingabekken (Fig. 3), a similar rise in $[\text{H}^+]$ with increased flow occurred, although observed pH has always been > 4.8 [8]. However, Al_i was estimated to be $< 1 \mu\text{M}$ under all flow conditions. Since Al_i was obtained by difference, using the Barnes/Driscoll method, negative values do occur in Fig. 3 and this reflects

the uncertainty in the method at these low levels of monomeric aluminium.

The differences between the three sites are highlighted by the plot of streamwater $[Al_i]$ versus $[H^+]$ (Fig. 4). The data shown are in all cases from the episode studies and, for Birkenes II, results are given for the four sampling stations along the main brook. For each of the three catchments the highest H^+ concentrations corresponded to highflow situations. Birkenes I, and to some extent

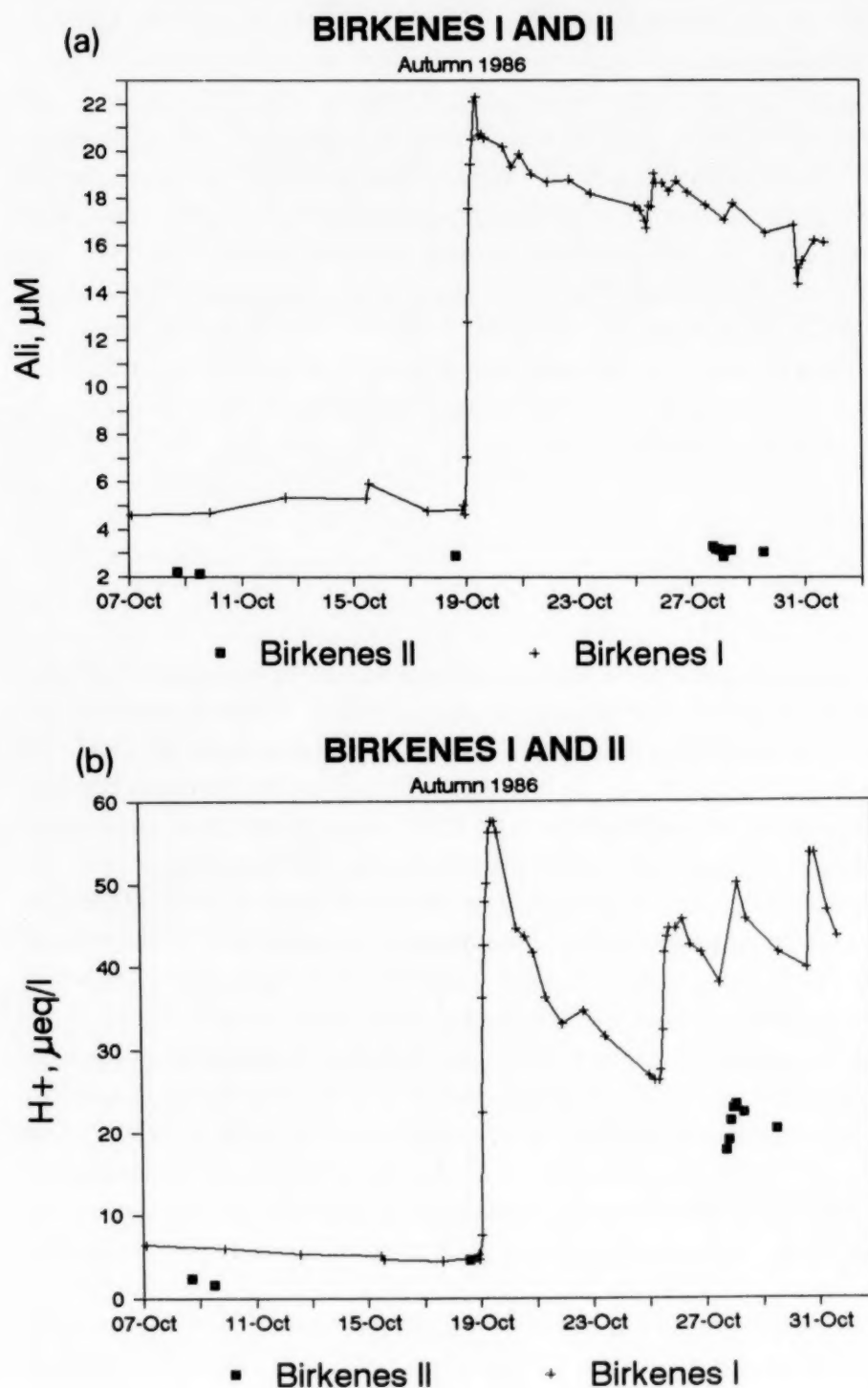
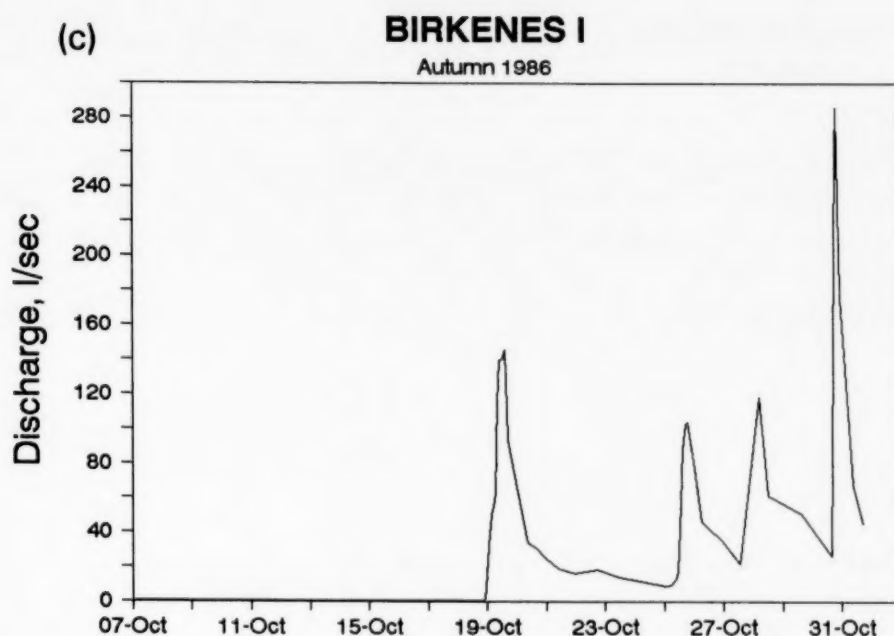


Fig. 2. Example of changes in streamwater chemistry during episodes for Birkenes I and II.



Birkenes II, showed a positive correlation between Al_i and H^+ , at least for lower concentrations. The sites cluster into three groups with Birkenes I being dominant both with respect to H^+ and Al_i followed by Birkenes II and Ingabekken. The Birkenes II samples have $[Al_i]$ in the range $3-4 \mu M$, which is close to the limit that freshwater fish can tolerate (e.g. ref. 16), this being consistent with the present fish status in the area. One could reasonably assume that the highflow chemistry at Birkenes I around 1950, when the fish disappeared, was similar to what is presently observed at Birkenes II. Total fluorine, which is a strong complexing agent for aluminium, was highest at Birkenes I followed by Birkenes II and negligible at Ingabekken (Table 2). The average organic monomeric aluminium, Al_o , was about $4 \mu M$ for both Birkenes I and II, while Ingabekken contained, on average, $2 \mu M$.

To illustrate differences in deposition and base cation release, excess SO_4 (i.e. the sulphate in excess of the seasalt contribution as computed from Cl) is plotted versus calcium for streamwater in Fig. 5. For excess sulphate (SO_4^*) the ranking between the catchments is the same as for Al_i . With respect to SO_4^* at Birkenes II, it is noteworthy that the two headwater sampling stations, unaffected by beaver activity, gave a higher average value of $96 \mu eq l^{-1}$ versus $77 \mu eq l^{-1}$ for the stations along the main brook (Table 2). For Birkenes I the average was $119 \mu eq l^{-1}$. The lower values for the main brook at Birkenes II could be caused by a combination of lower scavenging of gases and aerosols by the sparse deciduous forest, and sulphate reduction in the beaver bogs.

At all sites, Ca was inversely related to flow, and the ranges spanned can be seen in Fig. 5. Ingabekken showed both the lowest and highest Ca levels, which reflects the pronounced differences between highflow and lowflow composition [8]. Birkenes I and II were comparable with respect to calcium, implying a higher Ca/SO_4 ratio for the latter site.

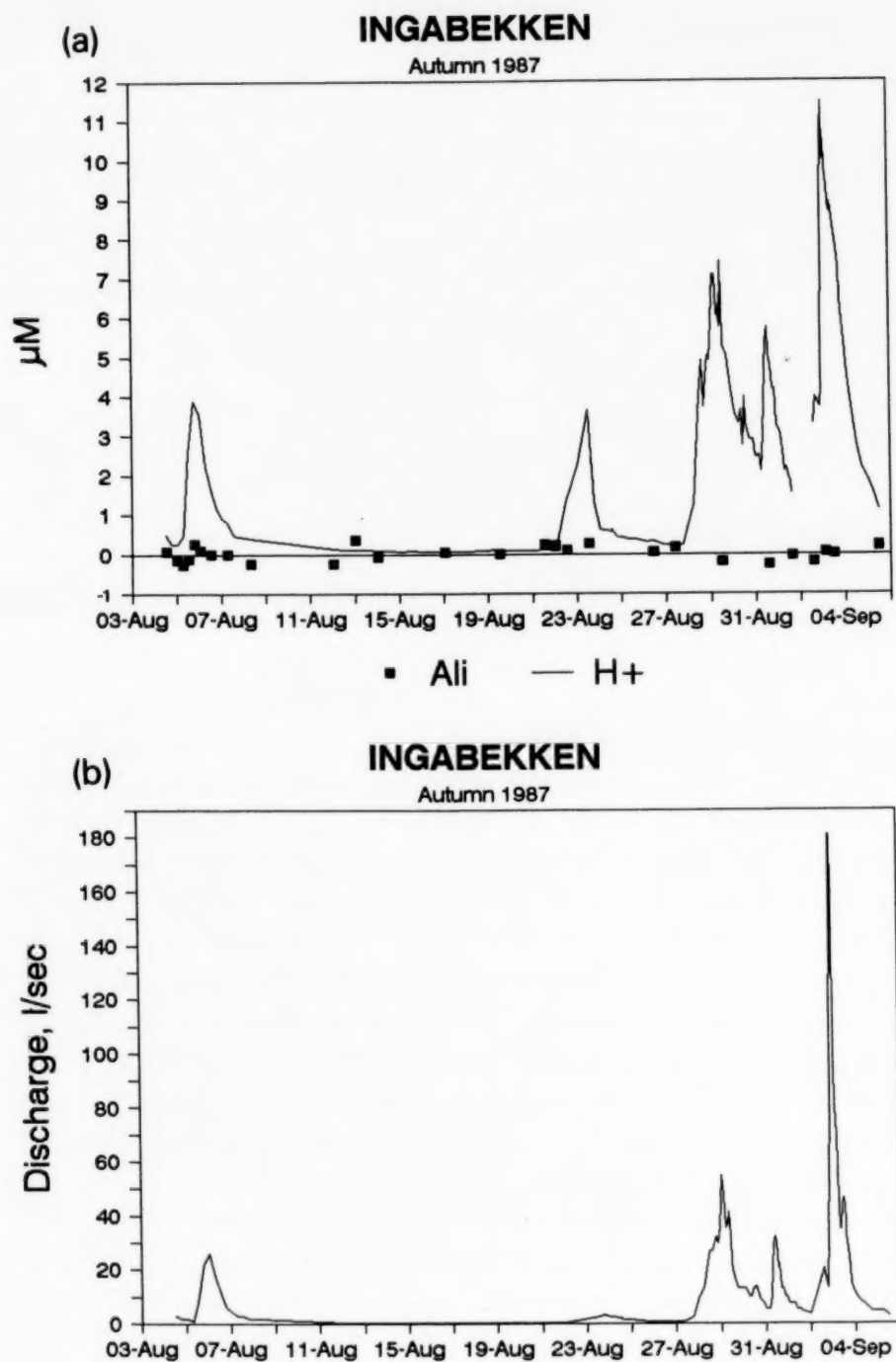


Fig. 3. Episodic changes in streamwater chemistry for Ingabekken.

Soil water chemistry

The Al_i and H^+ concentrations observed for streamwater were mirrored in the soil solution compositions (Table 3). At all sites the data show a vertical trend in the soil solution with decreasing H^+ and increased Ca levels with depth. Al_i increased with depth at Birkenes I and II, except for the horizon designated "Deep C" at Birkenes I. These samples are from separate lysimeters 2–3 m deep in the deposits along the brook where neutralization is probably

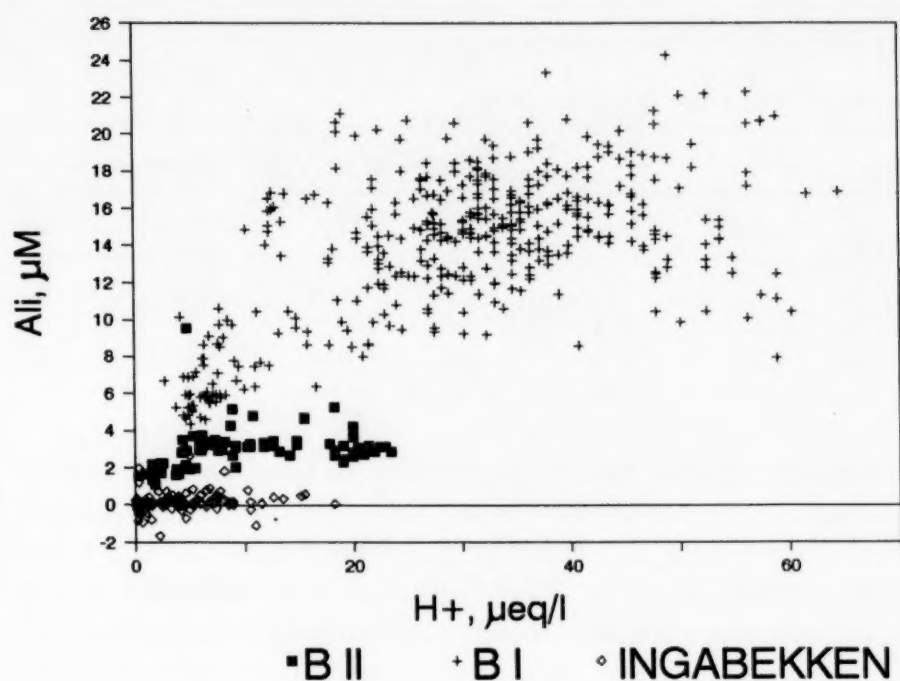


Fig. 4. Streamwater $[Al_i]$ versus $[H^+]$ for the three sites.

provided both from chemical reduction of sulphate ($[SO_4^{2-}] < 30 \mu eq l^{-1}$ in some cases) and release of base cations.

The soil solution concentrations of H^+ and Al_i at Birkenes I span the ranges of the streamwater samples (cf. Fig. 4 and Table 3). Thus, regarding these

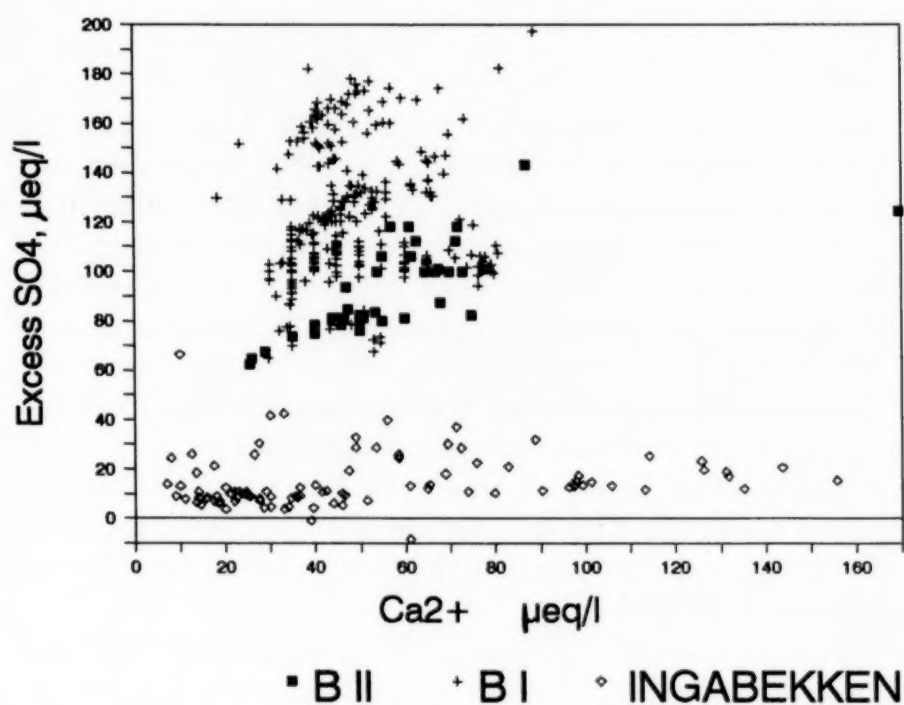


Fig. 5. Streamwater excess SO_4 concentrations versus $[Ca^{2+}]$ for the three sites.

TABLE 3

Median observed values for some major species in soil water

	Birkenes I				Birkenes II		Ingabekken	
	O/H	E	B/C	Deep C	O/H	B/C	Peat	Gley
Al _i (μ M)	8	25	32	4	6	8	< 0.1	< 0.1
H ⁺ (μ eq l ⁻¹)	78	45	33	0.9	4	0.1	2	0.6
Ca (μ eq l ⁻¹)	19	23	26	72	65	428	153	465

species, streamwater concentrations can be explained on the basis of mixing appropriate amounts of soil water; highflow being controlled by the O/H and B/C soil horizons and baseflow being regulated by the deeper deposits along the brook (cf. Neal and Christophersen [17]). At Birkenes II and Ingabekken the soil solution compositions do not span the observed streamwater chemistry in a similar way. This is presumably due to lack of detailed information because of the sparse instrumentation at these sites.

Excluding the "deep C" soil solution samples at Birkenes I, the observed vertical gradients in H⁺ and Al_i for this catchment suggest that neutralization of H⁺ is caused mainly by mobilization of aluminium and only to a modest extent by base cation release; a situation also reported from acidified catchments in Wales [18]. Birkenes II and Ingabekken provide more base-rich environments, but even at Birkenes II there is mobilization of aluminium in response to acid deposition.

Soil chemistry

Soil data for the three catchments are compared in Table 4 (A and B). To allow comparisons between catchments, results are given for more than one method. In comparing cation exchange capacity (CEC) and base saturation (BS) for Birkenes I and II (composite ammonium nitrate values) it is seen that CEC was similar, but BS was higher, at Birkenes II. Results in both cases are for podzolic soils on the slopes. Ingabekken [19] can only be compared with Birkenes I and the results for CEC and BS (ammonium acetate) are not considered to be significantly different. Similar results for soils on the slopes at Birkenes I (ammonium acetate) were obtained by Frank [15].

In the light of the differences in Al_i found in streamwater and soil water, exchangeable Al is given in Table 4B. The soils followed the ranking found in the other cases, with Birkenes I having the highest aluminium levels, succeeded by Birkenes II and Ingabekken.

Concluding the soil analyses, CEC is of comparable magnitude between sites, but the highest base saturation probably occurs at Birkenes II. Exchangeable aluminium does not follow the trend for base saturation, but decreases in the order Birkenes I, Birkenes II, and Ingabekken.

TABLE 4A

Comparison of cation exchange capacity, CEC (me/100 g), and base saturation BS (%). For Birkenes I and II the results are for podzolic soils. A composite sample represents a combined average of several single soil samples (see text)

	Birkenes I ^a					Birkenes II ^a					Ingabekken ^b	
	NH ₄ OAc		Composite NH ₄ NO ₃			NH ₄ OAc		Composite NH ₄ NO ₃			Composite NH ₄ OAc	
	CEC	BS	CEC	BS		CEC	BS	CEC	BS		CEC	BS
O	120	13	33	53	O			31	72	Peat	88	9
E	6	2	3	15	E	18	18	9	62	Gley	9	7
B	24	1	3	9	B	8	4	3	16			

^{a,b}See footnotes Table 4B.

TABLE 4B

Comparison of exchangeable aluminium (mg/100 g)

	Birkenes I Composite ^a			Birkenes II Composite ^a		Ingabekken Composite ^b
	NH ₄ NO ₃	KCl ^c		NH ₄ NO ₃	Peat Gley	
O	27.7		O	9.9		3.7
E	10.9	60	E	14.1		1.9
B	30.3	90	B	19.1		

^aNorwegian Forest Research Institute, Monitoring Programme for Forest Damage.^bChristophersen et al. [8].^cMulder et al. [7].

Implications

This study illustrates how aluminium is mobilized in two significantly different catchments in southern Norway as a response to acid deposition. Even in the relatively base-rich environment of Birkenes II, where total sulphur deposition also seems lower than at Birkenes I, proton neutralization occurs in part as aluminium release. This cannot be explained by the planting of spruce in one of the upper subcatchments of Birkenes II because the other adjacent and unaffected subcatchment shows the highest recorded Al_i values in streamwater (up to 8 μ M).

At Ingabekken, readily available inorganic aluminium is low throughout the catchment, even though soils are acidic and low in base cations. One can only speculate about the future of this catchment in the advent of acid deposition. However, given the low calcium levels at highflow for Ingabekken and the visible effects of acid deposition at Birkenes II, it is likely that Ingabekken would respond in a similar way (cf. Anderson et al. [11], who compared the Høylandet area with acidified Scottish catchments).

Under these circumstances, Ingabekken highflow chemistry could be representative for pristine conditions during stormflow in southern Norway. In this connection, the similar TOC levels in streamwater at all three sites ($\sim 4 \text{ mg l}^{-1}$, Table 2) are noteworthy. This finding, together with the lack of available aluminium at Ingabekken, point against the hypothesis put forward by Krug and Frink [20]. They assumed that freshwaters in granitic areas were naturally acidic due to organic acids, and that the impact of acid deposition was substitution by strong mineral acids followed by reduced TOC levels, without much change in other respects.

A potentially large source of aluminium is the predominantly organically-bound aluminium stores built up in the Bs horizons during soil genesis (cf. refs 11 and 21). On solubilization, the aluminium in the soil will move with the soil water and contact upper organic layers further down the hillslope, particularly when the slopes are water saturated. Under pristine conditions the aluminium

will be tightly bound by organic matter in the upper soil layers but, as the transfer of aluminium from the B to the O/H horizons increases during acidification, organic matter will be transformed from a cation exchanger dominated by H^+ to one where Al plays an increasingly important role.

None of the presently used acidification models allow for processes as depicted here. For example, neither the Birkenes model, ILWAS, nor MAGIC include: (i) the transfer of water from the weathering zones (B and C horizons) back into the organic horizon; and (ii) the gradual increase in exchangeable aluminium over H^+ on the exchange complex. Also, aluminium release in acidification models is generally based on dissolution of an $Al(OH)_3$ mineral, neglecting the store of organically bound aluminium (cf. Stone and Seip, [3]). In this context, modifications of the existing models, as well as new initiatives, should be encouraged. Developments along the lines taken by van Grinsven [22] and Tipping and Hurley [23] are advocated; in the former case the ILWAS model was modified to allow for H^+ and Al exchange, while in the latter case the CHAOS model depicts cation exchange for the organic soils using more appropriate equilibrium formulations than any used in the present models.

ACKNOWLEDGEMENTS

This work was funded by the joint British-Scandinavian Surface Water Acidification Programme (SWAP), the Royal Norwegian Council for Scientific and Industrial Research (NTNF), and the Norwegian Department of the Environment. Valuable comments were received from Hans M. Seip, and field assistance is gratefully acknowledged from Dag Olav Andersen and Rune Skaane.

REFERENCES

- 1 S. Gherini, L. Mok, R.J.M. Hudson, G.F. Davis, C. Chen and R. Goldstein, The ILWAS model: Formulation and application, *Water, Air Soil Pollut.*, 26 (1985) 95-113.
- 2 N. Christophersen, H.M. Seip and R.F. Wright, A model for streamwater chemistry at Birkenes, Norway, *Water Resour. Res.*, 18 (1982) 977-996.
- 3 A. Stone and H.M. Seip, Mathematical models and their role in understanding water acidification: An evaluation using the Birkenes model as an example, *Ambio*, 18 (1989) 192-199.
- 4 B.J. Cosby, G.M. Hornberger, J.N. Galloway and R.F. Wright, Modelling the effects of acid deposition: Assessment of a lumped parameter model of soil and streamwater chemistry, *Water Resour. Res.*, 21 (1985) 51-63.
- 5 J.O. Reuss, N. Christophersen and H.M. Seip, A critique of models for freshwater and soil acidification, *Water, Air Soil Pollut.*, 30 (1986) 909-930.
- 6 H.M. Seip, D.O. Andersen, N. Christophersen, T.J. Sullivan and R.D. Vogt, Variations in concentrations of aqueous aluminium and other chemical species during hydrological episodes at Birkenes, southernmost Norway, *J. Hydrol.*, 108 (1989) 387-405.
- 7 J. Mulder, N. Christophersen, M. Hauhs, R.D. Vogt, S. Andersen and D.O. Andersen, Hydrological controls in the Birkenes catchment as inferred from a rainstorm high in seasalts, *Water Resour. Res.* (1989)(in press).
- 8 N. Christophersen, R.D. Vogt, C. Neal, H.A. Anderson, R.C. Ferrier, J.D. Miller and H.M. Seip, Controlling mechanisms for streamwater chemistry at the pristine Ingabekken site in

- mid Norway: Some implications for acidification models, *Water Resour. Res.*, 27 (1990) 59–67.
- 9 SFT, Norwegian State Pollution Control Authority, Monitoring of Long Range Transported Air and Precipitation, Report 296/87, Oslo, 1987, 199 pp. (in Norwegian with English summary).
 - 10 A. Semb, A comparison between precipitation quality at Tustervatn and Høylandet, Norwegian Institute for Air Research, 1987, 10 pp. (in Norwegian).
 - 11 H.A. Anderson, R.C. Ferrier and J.D. Miller, The surface water acidification programme — A comparison between the pristine Høylandet and the polluted Loch Chon sites, *Ambio* (in press).
 - 12 T.J. Sullivan, N. Christophersen, I.P. Muniz, H.M. Seip and P.D. Sullivan, Aqueous aluminium chemistry response to episodic increases in discharge, *Nature*, 323 (1986) 324–327.
 - 13 C.T. Driscoll, A Procedure for the fractionation of aqueous aluminium in dilute acidic waters, *Int. J. Environ. Anal. Chem.*, 16 (1984) 267–283.
 - 14 T.J. Sullivan, H.M. Seip and I.P. Muniz, A comparison of frequently used methods for the determination of aqueous aluminium, *Int. J. Environ. Anal. Chem.*, 26 (1986) 61–75.
 - 15 J. Frank, Soil survey at Birkenes, a small catchment in Aust Agder county, southern Norway, SNSF Project TN 60/80, Norwegian Institute for Water Research, Oslo, 1980, 41 pp.
 - 16 SFT, Norwegian State Pollution Control Authority, 1000 lake survey 1986 — Fish status, Report 313/88, Oslo, 1988, 35 pp.
 - 17 C. Neal and N. Christophersen, Inorganic aluminium–hydrogen ion relationships for acidified streams; the role of water mixing processes, *Sci. Total Environ.*, 80 (1989) 195–203.
 - 18 C. Neal, B. Reynolds, P. Stevens and M. Hornung, Hydrogeochemical controls for inorganic aluminium in acidic stream and soil waters at two upland catchments in Wales, *J. Hydrol.*, 106 (1989) 155–175.
 - 19 Macaulay Land Use Research Institute, Soil Survey at Høylandet, Internal Report, Aberdeen, 1988.
 - 20 E.C. Krug and C.R. Frink, Acid rain and acid soil: A new perspective, *Science*, 221 (1983) 520–525.
 - 21 J. Mulder, N. van Breemen and H.C. Eijck, Depletion of soil aluminium by acid deposition and implications for acid neutralization, *Nature*, 337 (1989) 242–249.
 - 22 J.J.M. van Grinsven, The ILWAS model to analyse the response of an acid forest soil to acid deposition and mitigation measures, Doctoral thesis, Agricultural University of Wageningen, 1988, pp. 131–160.
 - 23 E. Tipping and M.A. Hurley, A model of solid–solution interactions in acid organic soils, based on the complexation properties of humic substances, *J. Soil Sci.*, 39 (1988) 505–520.
 - 24 A.O. Stuanes, G. Ogner and M. Opem, Ammonium nitrate as extractant for soil exchangeable cations, exchangeable acidity and aluminum, *Commun. Soil Sci. Plant Anal.*, 15 (1984) 773–778.

EFFECT OF NITROGEN ON DROUGHT RESISTANCE OF NORWAY SPRUCE AND SCOTS PINE

PETTER NILSEN

Norwegian Forest Research Institute, Division of Forest Ecology, P.O. Box 61, N-1432 Ås-NLH (Norway)

ABSTRACT

Six fertilization experiments in mature spruce and pine stands were analyzed for growth response during two successive extremely dry summers, to evaluate the hypothesis that nitrogen deposition increases canopy growth and water demand, leaving the trees less drought resistant. Nitrogen had been applied at rates varying from a single application of 150 kg ha^{-1} , up to repeated applications of 600 kg ha^{-1} . The last application was 2–5 years before the drought. In two experiments, growth showed a slight depression during one of the two dry years, compared with what would be expected as normal. The growth depression was rather small and absolute growth was far greater than that of the control trees. In the other four experiments, no signs of deviation from normal growth were detected. The study indicates that the present level of nitrogen deposition in southern Norway has not significantly reduced the drought resistance of spruce and pine forests.

INTRODUCTION

During the last decades, the deposition of nitrogen has increased in most parts of the world. In southern Norway, wet deposition of nitrogen varies from ~ 5 to $15 \text{ kg ha}^{-1} \text{ year}^{-1}$. The most important nitrogen components of acid rain are nitrate and ammonium ions.

In addition, dry deposition adds a quantity varying from a few percent to $> 100\%$ of the wet deposition. In Norway, estimates between 15 and 30% are common. The amount of dry deposition depends largely on vegetation and distance from the source of emission (Andersen, 1986).

Good estimates of total nitrogen loads in heavily polluted areas can be achieved from measurements of throughfall in forest stands, although leaching of nutrients from needles or leaves will contribute to the estimates. In the Netherlands, a throughfall of $> 150 \text{ kg N ha}^{-1} \text{ year}^{-1}$ has been reported in Douglas fir stands (Ivens et al., 1987).

Such quantities certainly affect soil and vegetation. A common view is that nitrogen in moderate quantities has a positive effect on tree growth and vigour. Fertilization experiments in many countries have demonstrated a growth-promoting effect of nitrogen application on several tree species. Doses of up to 150 and 200 kg N ha^{-1} are used in commercial forestry. The fertilization is carried out once, or repeated at intervals of 6–8 years. Thus the most polluted

areas receive far more nitrogen than would have been the case under a commercial fertilization program. In the southern parts of Norway, the amount of nitrogen from deposition represents about one-half that prescribed in an intensive fertilization program with repeated application.

Concern has been expressed about the possible negative effects of heavy loads of nitrogen on ecosystems and forest growth (Nihlgård, 1985; Mohr, 1986; Mohren et al., 1986; Lindroth, 1987). Such effects are:

- increased canopy growth, leading to a higher water demand and thereby greater susceptibility to drought stress;
- a relative shortage of other elements, especially magnesium, potassium, phosphorus, and, in some cases, boron;
- high concentrations of nitrogen in the soil can negatively affect mycorrhiza, leading to impaired uptake of phosphorus by the trees.

The following discussion will concern drought resistance of spruce and pine. In this context, drought resistance is a measure of a tree's ability to withstand a drought period without suffering severe growth reduction or death.

Increased nitrogen deposition and drought resistance

One possible effect of nitrogen deposition is that increased canopy growth will increase the tree's demand for water. In a given soil, the water available for plant growth will thus be depleted sooner. This could result in shedding of older leaves and a decrease in crown density, a common feature in the "forest decline" syndrome. The top/root ratio will probably also increase due to greater nitrogen availability, as shown in fertilization experiments in young pine (Linder and Axelsson, 1982). During severe drought periods the ability of the roots to supply a larger crown with water could possibly be restricted, even if water is available deeper in the soil profile.

Support for the hypothesis

Experiments with pine seedlings (*Pinus contorta*) show a decline in drought resistance with increasing nitrogen fertilization (Etter, 1969). Others have found an optimum nitrogen level for drought resistance (e.g. in *Pinus banksiana* and *P. taeda*), leaving nitrogen-deficient plants and plants with an over-optimal nitrogen regime least resistant (Bensend, 1943; Pharis and Kramer, 1964).

In a 10-year-old plantation of fast-growing *Pinus radiata* in Australia, greater mortality and lower productivity appeared in fertilized plots during a severe drought period (Linder et al., 1987). One year before the drought period, 400 kg N ha⁻¹ had been applied.

On the other hand, fertilized 20-year-old Scots pine in Sweden showed less negative water potentials during a dry period than non-fertilized trees, indicating less stress in the fertilized trees (Hillerdal-Hagströmer et al., 1982).



Fig. 1. The geographical location of the experiments and the climate stations in southeast Norway.

The purpose of this preliminary investigation was to analyze the growth response in Norwegian fertilization experiments during the dry summers of 1975 and 1976, searching for possible deviations from a normal growth pattern in fertilized trees. The summer precipitation (3 months) in these years varied from 65 to 170 mm for some selected stations. This corresponds to approximately 20–65% of the normal summer precipitation.

TABLE 1

Precipitation (mm) and percentage of normal period (1931–60) from selected stations. The stations are situated in the same climatic regions as the fertilization experiments. Data from The Norwegian Meteorological Institute (1975–1976)

Station	Year	June		July		August	
		mm	(%)	mm	(%)	mm	(%)
Tynset (Exp. 940, 941)	1975	19	(31)	24	(31)	33	(57)
	1976	59	(95)	41	(53)	30	(52)
Flisa (Exp. 803, 932)	1975	24	(35)	73	(84)	50	(60)
	1976	36	(53)	57	(66)	20	(24)
Kise (Exp. 801)	1975	17	(27)	47	(57)	50	(71)
	1976	36	(57)	54	(66)	18	(26)
Byglandsfjord (Exp. 881)	1975	41	(48)	73	(70)	55	(43)
	1976	26	(31)	40	(38)	0	(0)

MATERIALS

Six fertilization experiments were selected from a large number of old field trials. Fertilization had been carried out 2–5 years before the dry years of 1975 and 1976. Thus the drought would fall within the period of maximum growth response. All trials were located in southeast Norway (Fig. 1). Four involved Scots pine and two Norway spruce. Growth data are taken from a comprehensive summary of the fertilization experiments of the Norwegian Forest Research Institute (Sture, 1984). The growth in fertilized plots was calculated as a percentage of the controls. The summer precipitation (in mm and as a percentage of normal values) is presented in Table 1.

RESULTS

Scots pine

Figure 2 shows the volume growth response of fertilized plots compared with control plots (100%) in a Scots pine stand (Experiment 803). The growth response shows a decrease for both fertilization treatments in 1975, but not in 1976. The decrease, however, is rather small and the absolute growth of the trees was far ahead of that of the control trees.

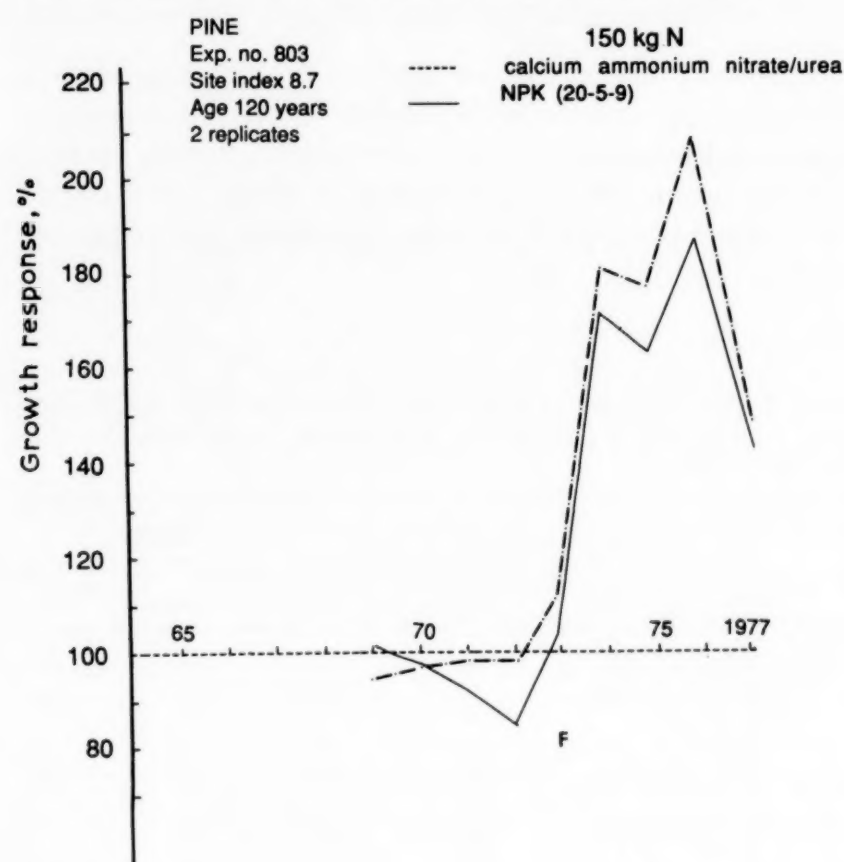


Fig. 2. Volume growth response (%) in Experiment 803 with Scots pine. F indicates year of fertilization. Site index means dominant tree height (m) at age 40 years in breast height. The calcium ammonium nitrate and urea replicates are treated together.

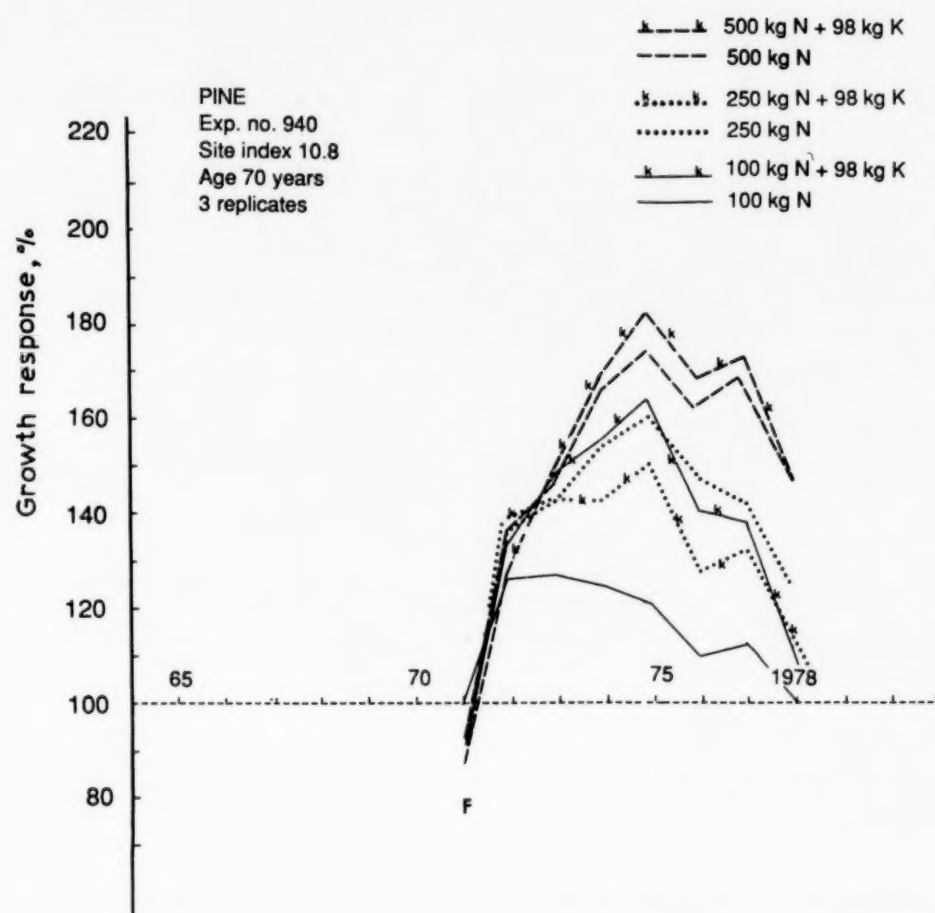


Fig. 3. Volume growth response (%) in Experiment 940 with Scots pine. Fertilizer: Calcium ammonium nitrate and potassium (KCl), kg N and K ha⁻¹.

Figure 3 shows results from another fertilization experiment with pine (Experiment 940). There is a decrease in growth response in 1976 in nearly all treatments compared with the control. The drop in response is rather small, and here also the growth is far greater than that of the control. In Experiment 941 (Fig. 4) situated nearby on the same type of soil, there is no unusual pattern in growth response during the period.

Figure 5 shows results from the last experiment with pine (Experiment 881). The responses to the second fertilization were rather small with the heaviest treatment. No irregular decrease in growth response compared with the untreated control can be detected during the dry years.

Norway spruce

Growth response in the spruce stands is shown in Figs 6 and 7. No irregular decrease in growth response can be seen in these experiments.

DISCUSSION

In a stress situation the carbohydrate production of trees decreases and

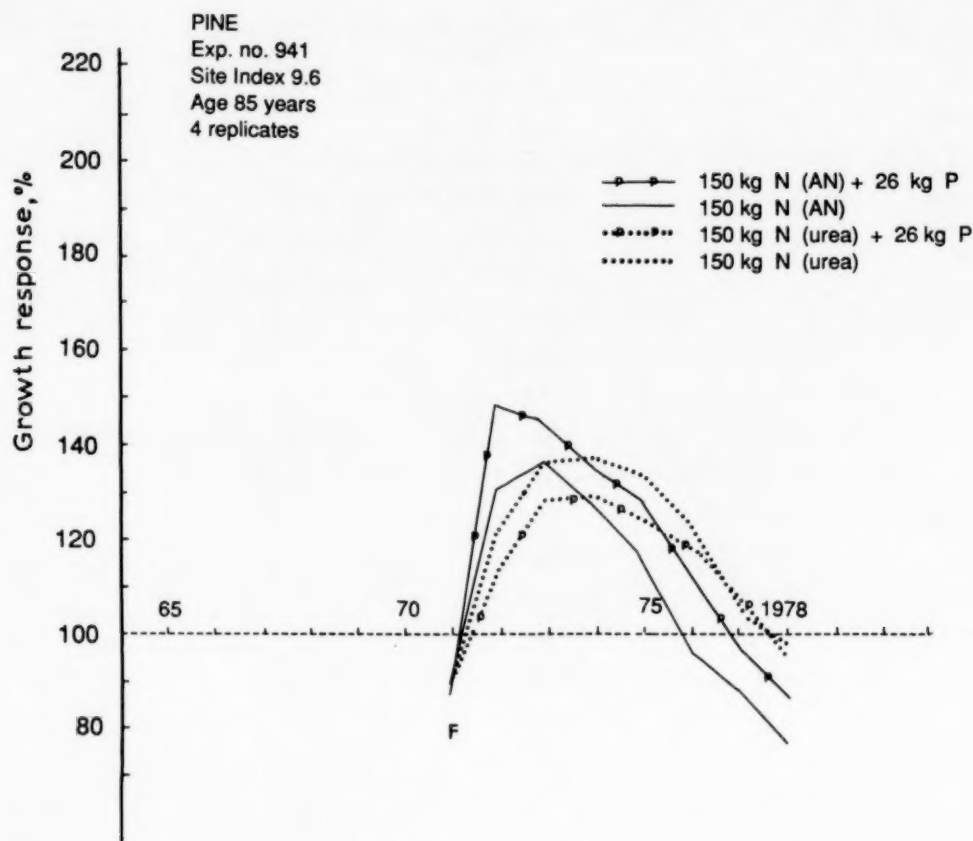


Fig. 4. Volume growth response (%) in Experiment 941 with Scots pine. AN is calcium ammonium nitrate, kg N and P ha^{-1} .

supplies gradually become more and more restricted. Carbohydrate allocation for supportive tissues such as annual rings has a relatively low priority in the trees (Ericsson et al., 1980; Waring, 1987). It is, therefore, very likely that increased drought-induced stress of fertilized trees could be detected in their growth response.

In a closed forest stand the needle biomass will reach an upper level, restricted by, among other factors, the nutritional state of the site (Axelsson, 1983). If nitrogen is the most limiting factor, which is usually the case in boreal coniferous forests, application of nitrogen will lead to an increase in needle biomass or leaf area (LA). This increase will result in a larger total production, mostly allocated to "above-ground" biomass.

To detect possible stress effects of drought in fertilization experiments, one has to look at periods of growth response when the trees have a larger LA and an altered carbohydrate allocation. It is, therefore, not very likely that a large decrease in growth response in Experiment 881 would occur. In this stand, the response to the second fertilization is fairly small in 1975–76. The first heavy application of nitrogen (600 kg ha^{-1}) may have resulted in nitrogen saturation. This means that the vegetation will not respond with increased growth to further nitrogen application. A relative deficiency of other elements, such as phosphorus, could also be a possible explanation of the lack of growth response (Aronsson, 1985; Möller 1985; Meijer, 1986).

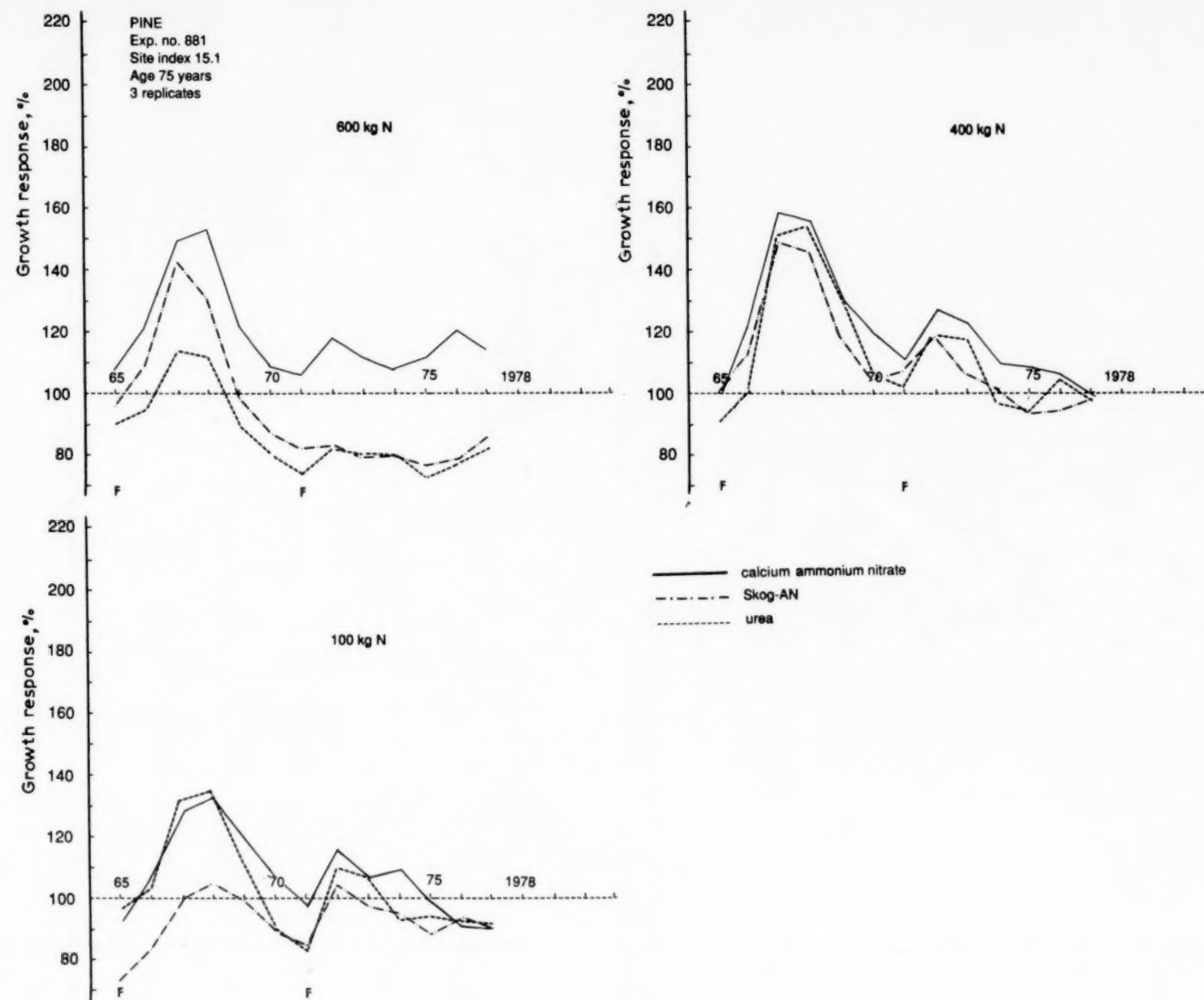


Fig. 5. Volume growth response (%) in Experiment 881 with Scots pine. Skog-AN is granulated ammonium nitrate, kg N ha^{-1} .

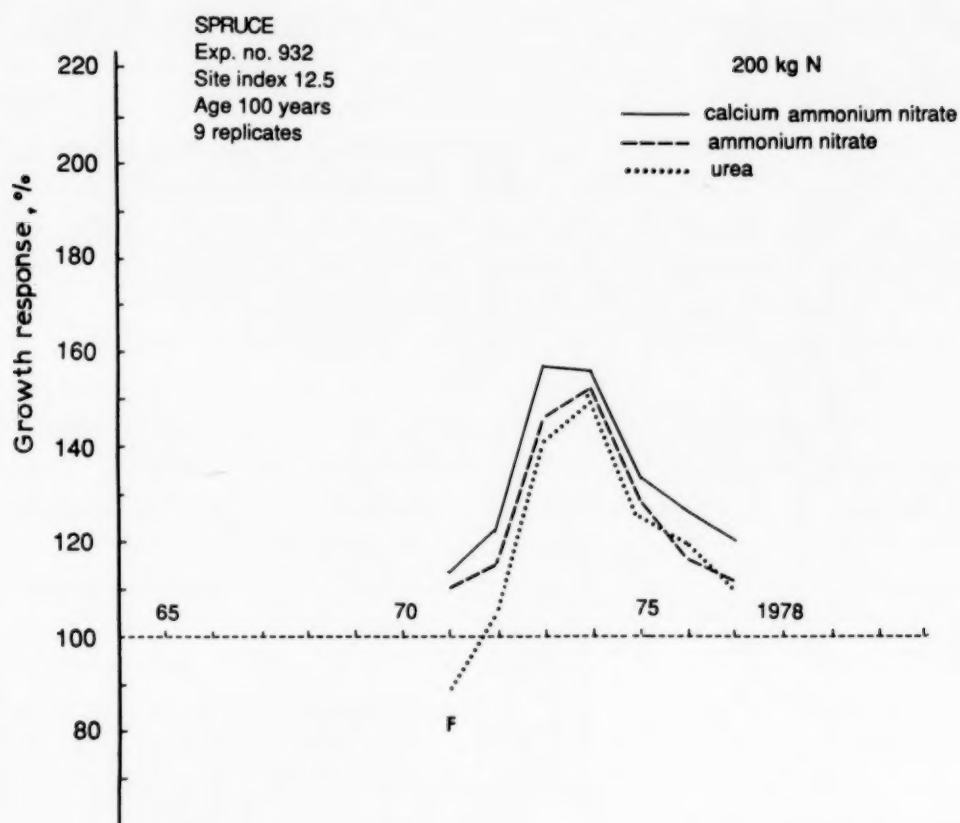


Fig. 6. Volume growth response (%) in Experiment 932 with Norway spruce. Curves are the mean of nine replicates with the same amount of nitrogen, but some plots received 30 or 50 kg P ha⁻¹.

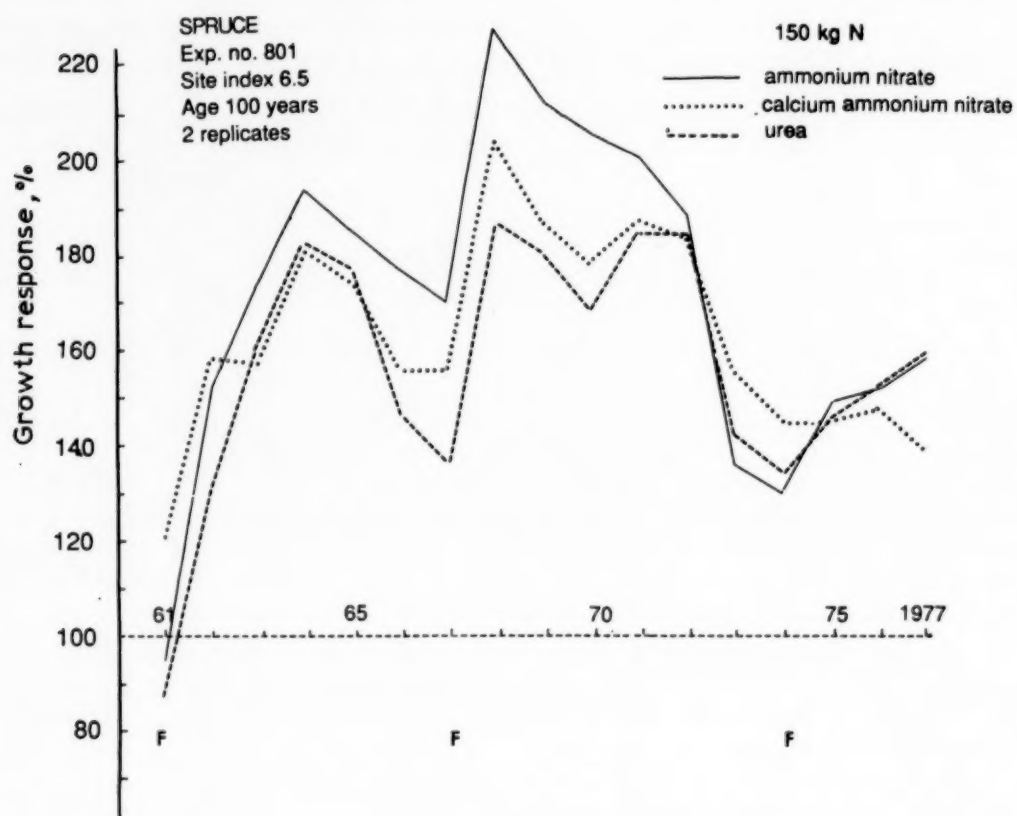


Fig. 7. Volume growth response (%) in Experiment 801 with Norway spruce.

The results from Experiments 803 and 940 give a slight indication that the effect of drought can be more serious in a fertilized stand than elsewhere. The deviation from the expected or normal response is, however, fairly small. In Experiment 940, even plots with a small application of nitrogen show a decrease in response. This strongly indicates that the growth depletion in this experiment is just a coincidence. Experiment 941, which is situated nearby on the same type of soil, shows no drop in response. The conditions of these plots would be expected to be very similar.

A major problem in analyzing these experiments is the lack of knowledge concerning relations with water. As seen from Table 1, typical monthly precipitation was from 20 to 50 mm, representing only 25–60% of normal values. Unfortunately, no observations of groundwater level or physical soil properties in the experimental areas were made. These factors are of overall importance for root morphology and water availability of the trees. Roots of spruce and pine have been shown to penetrate glacial sediment to a depth of > 3 m to collect groundwater (Bjor and Huse, 1987).

Another problem is the validity of extrapolating results from fertilization experiments, with few applications of large amounts of nitrogen, to the polluted situation, with small amounts but almost continuous application. A small and frequent nitrogen application is probably less likely to increase the risk of damage caused by drought (Linder et al., 1987).

CONCLUSION

The growth responses in some Norwegian fertilization experiments show no dramatic decrease during the severe drought periods of 1975–76. This indicates that the present level of nitrogen deposition in southern Norway has not led to significantly reduced drought resistance in spruce and pine forests of these areas.

REFERENCES

- Andersen, B., 1986. Impact of nitrogen deposition. In: J. Nilsson (Ed.), *Critical Loads for Nitrogen and Sulphur*. Nordisk Ministerråd, Miljörapport 1986, 11: 159–197.
- Aronsson, A., 1985. Indikationer på stress vid obalans i trädens växtnäringsinnehåll. K. Skogs-Lantbruksakad. Tidskr., Suppl., 17: 40–51.
- Axelsson, B., 1983. Fordelning av trädets nettoproduktion på stam, grenar, blad och rötter. Skogsfakta, Suppl., 2: 24–29. Det biologiska taket för Skogsproduktion. Skogshögskolans höstkonferens, 1982.
- Bensend, D.W., 1943. Effect of nitrogen on growth and drought resistance of jack pine seedlings. Univ. Minn. Agric. Exp. Stn Tech. Bull., 163, 63 pp.
- Bjor, K. and M. Huse, 1987. Soil temperature variations at the field station Nordmoen. Medd. Nor. Inst. Skogforsk, 40(2): 1–12.
- Ericsson, A., S. Larsson and O. Tenow, 1980. Effects of early and late defoliation on growth and carbohydrate dynamics in Scots pine. J. Appl. Ecol., 17: 747–769.
- Etter, H.M., 1969. Growth, metabolic components and drought survival of lodgepole pine seedlings at three nitrate levels. Can. J. Plant Sci., 49: 393–402.
- Hillerdal-Hagströmer, K., E. Mattson-Djos and J. Hellkvist, 1982. Field studies of water relations

- and photosynthesis in Scots pine. II. Influence of irrigation and fertilization on needle water potential of young pine trees. *Physiol. Plant.*, 54: 295-301.
- Ivens, W.P.M.F., G.P.J. Draaijers and W. Bleuten, 1987. Atmospheric nitrogen deposition in a forest next to an intensively used agricultural area. In: P. Mathy (Ed.), *Air Pollution and Ecosystems. Proc. Int. Symp.*, Grenoble, France 18-22 May 1987. Reidel, Dordrecht, pp. 536-541.
- Linder, S. and B. Axelsson, 1982. Changes in carbon uptake and allocation patterns as a result of irrigation and fertilization in a young *Pinus sylvestris* stand. In: R.H. Waring (Ed.), *Carbon Uptake and Allocation in Subalpine Ecosystems as a Key to Management*. Forest Research Laboratory, Oregon State University, Corvallis, OR, pp. 38-44.
- Linder, S., M.L. Benson, B.J. Myers and R.J. Raison, 1987. Canopy dynamics and growth of *Pinus radiata*. I. Effects of irrigation and fertilization during a drought. *Can. J. For. Res.*, 17: 1157-1165.
- Lindroth, A., 1987. Kvävetillförsel kan orsaka kronutglesning. *Sven. Skogsvårdsfören. Tidskr.*, 3: 9-17.
- Meijer, K., 1986. Critical loads for sulphur and nitrogen deposition in the Netherlands. In: J. Nilsson (Ed.), *Critical Loads for Nitrogen and Sulphur*. Nordisk Ministerråd, Miljörapport 1986, 11: 223-232.
- Mohr, H., 1986. Die Erforschung der neuartigen Waldschäden. *Biol. Unserer. Zeit.*, 16(3): 83-89.
- Mohren, G.M.J., J. van den Burg and F.W. Burger, 1986. Phosphorus deficiency induced by nitrogen input in Douglas fir in the Netherlands. *Plant Soil*, 95: 191-200.
- Möller, G., 1985. Results from forest fertilization field trials in areas with high nitrogen input. In: J. Nilsson (Ed.), *Nitrogen Saturation. Abstracts from a Workshop*, Uppsala, 1 Oct. 1985. Statens Naturvårdsverk, Rapp. 3153, pp. 49-61.
- Nihlgård, B., 1985. The ammonium hypothesis — an additional explanation to forest dieback in Europe. *Ambio*, 14(1): 2-8.
- Pharis, R.P. and P.J. Kramer, 1964. The effects of nitrogen and drought on loblolly pine seedlings. I. Growth and composition. *For. Sci.*, 10(2): 143-150.
- Sture, S., 1984. Gjødlingsforsøk i gran- og furuskog. Norwegian Forest Research Institute, 528 pp.
- Waring, R.H., 1987. Characteristics of trees predisposed to die. *BioScience*, 37(8): 569-574.

LEAD AND CADMIUM CONTAMINATION OF SOIL AND VEGETABLES IN THE UPPER SILESIA REGION OF POLAND

JADWIGA GZYL

Institute of Environmental Protection, Kossutha 6, 40-832 Katowice (Poland)

ABSTRACT

Studies of the lead and cadmium content of soils and vegetables from 126 allotments in 12 towns in a polluted region of Poland are described. Metal concentrations in parsley, celery, carrots and red beet were determined using AAS. In most cases, metal concentrations in soils and vegetables exceeded accepted standards and concentrations found in rural regions.

A total of 756 vegetable samples were studied and only 170 met the standard for lead and 17 for cadmium. The lowest lead content was found in parsley roots and the highest in celery leaves. Cadmium content between species did not differ greatly and the highest concentrations were recorded for celery.

The metal intake by the consumer was also calculated using questionnaire data concerning vegetable consumption. In relation to the reference area, the metal intake in the polluted area was 2–5 times higher for lead and 2–16 times higher for cadmium. The main species responsible for the high metal concentrations were carrots and red beet.

Replacing carrots and red beet with the same species grown in an unpolluted region would reduce the consumer's metal intake from vegetables considerably.

INTRODUCTION

The level of industrialization in the Upper Silesia region is the highest in Poland. About 1000 industrial plants are located there, out of which 200 have a large negative effect upon the environment. Industrial complexes include mines, smelters, and power, coke and chemical plants.

In some parts of Katowice District, the level of metals in the soil is related not only to air deposition but also to the natural occurrence of lead, zinc and cadmium in soils. Studies were carried out in 1982 and 1983 to determine the level of metals in soils and vegetable samples from over 100 allotments. The project was part of a large survey completed for Katowice District by the Institute of Environmental Protection (Kucharski et al., 1982, 1983, 1984 a,b; Marchwińska et al., 1983).

MATERIALS AND METHODS

Each allotment, which is publicly-owned land rented to private individuals, consists of approximately 200 plots. Soil and vegetables from 15 to 20 plots and from 6 to 8 sampling sites within each plot were taken from all allotments.

Soil samples of ~ 0.3 kg were collected using an Egner sampling stick and then crushed, mixed and air-dried at 60°C . After drying, 1–5 g of soil was placed in an Erlenmeyer flask and shaken with 25 ml of an extraction solution consisting of 10% HNO_3 . The acid suspension was filtered and washed with double distilled water.

Vegetable samples were washed with tap water and peeled. Lead and cadmium concentrations in tap water were low, 0.008 and 0.001 mg dm^{-3} , respectively. No increase in metal concentration due to tap water was observed. The air-dried material was ground, weighed and incinerated in porcelain crucibles at 400°C for 24 h. The ash was treated with 20% HCl and incinerated for an additional 24 h at 400°C . The dry residue was dissolved in 2.5 ml of 20% HCl and filtered.

Metal concentrations both in soils and vegetables were determined by AAS using a Varian Techtron Model AA5 spectrometer at wavelengths 217.0 and 228.8 nm for lead and cadmium, respectively.

Statistical analyses showing the accuracy of the method for determination of these metals in plant material are presented in Table 1.

Parsley, celery, carrots and red beet were selected for evaluation because of their tendency to accumulate metals and also on account of their contribution to the local diet.

RESULTS

The results of our investigations are presented in Table 2. Soils in the allotments are heavily influenced by anthropogenic activities. The structure is typical for garden soils. Organic and macroelemental contents are relatively high, while pH is close to neutral.

Lead concentrations in the soils ranged from 16.8 to 1640 mg kg^{-1} with a mean of 221.4 mg kg^{-1} . The cadmium values ranged from 1.20 to 51.70 mg kg^{-1} with a mean of 8.30 mg kg^{-1} . For vegetables, the lowest lead concentration was found in parsley roots and the highest in celery leaves. The highest concentrations of cadmium were found in celery.

DISCUSSION

The lead content of agricultural soils does not usually exceed 50 mg kg^{-1} . The cadmium content is generally not higher than 1 mg kg^{-1} (Kabata-Pendias and Pendias, 1979; Archer, 1980; Bennet, 1981). Soil samples collected from allotments in Katowice District exhibited concentrations 50 times higher than those from unpolluted areas. In Poland, the maximum allowable concentrations for cadmium and lead in light soils are 3 and 50 mg kg^{-1} , respectively. In heavy soils, the value for lead increases to 100 mg kg^{-1} (Monitor Polski, 1986). This maximum allowable concentration is exceeded many times in Katowice District. The concentrations presented above are comparable to values reported for other studies carried out in the vicinity of non-ferrous metal

TABLE 1

Statistical analysis of lead and cadmium concentrations in plant material

		Lead content (mg kg ⁻¹ dry wt)		Cadmium content (mg kg ⁻¹ dry wt)	
		Leaves	Roots	Leaves	Roots
Number of samples		20	20	20	20
Range	NF	8.09–9.41	3.78–4.47	2.243–2.657	1.596–1.660
	F	10.81–12.43	6.53–7.52	3.108–3.678	2.305–2.705
Arithmetic mean	NF	8.75	4.14	2.450	1.622
	F	11.62	7.03	3.336	2.509
Standard deviation	NF	0.63	0.30	0.199	0.135
	F	0.78	0.47	0.255	0.197
Coefficient of variation	NF	7.2	7.2	8.1	8.3
	F	6.7	6.7	7.6	7.8
Error of method (%)		4.3	3.7	11.4	11.3
Recovery of added metal (%)		95.7	96.3	88.6	88.7

NF, samples without standard; F, samples with standard (3 mg Pb kg⁻¹ plant material or 1 mg Cd kg⁻¹ plant material).

TABLE 2

Lead and cadmium concentrations in soil and vegetables from 126 allotments

Statistical parameter	Lead (mg kg ⁻¹ dry wt)							Cadmium (mg kg ⁻¹ dry wt)							Soil pH
	Soil	Vegetables						Soil	Vegetables						
		Parsley		Celery		Carrot roots	Red beet roots		Parsley		Celery		Carrot roots	Red beet roots	
		Leaves	Roots	Leaves	Roots				Leaves	Roots	Leaves	Roots			
Minimum	16.8	1.3	1.0	3.5	1.0	1.0	1.0	1.2	0.30	0.20	0.21	0.70	0.70	0.30	5.00
Maximum	1640.8	49.5	9.6	47.3	10.6	9.4	16.1	51.7	13.50	2.35	19.33	10.88	5.25	5.90	7.50
Mean	221.4	7.9	2.7	9.5	3.2	2.7	2.6	8.3	0.97	0.57	2.82	2.21	1.06	0.97	7.01

TABLE 3

Lead concentrations in vegetables relative to the standard

Vegetables		Relative amount ^a		Number of samples not exceeding the standard
		Maximum	Mean	
Parsley	leaves	27	4	3
	roots	7	2	19
Celery	leaves	21	4	
	roots	5	1.5	33
Carrot	roots	3	1.2	67
Red beet	roots	7	1.2	58

^aObserved concentration divided by the standard concentration.
Number of samples, 756.

smelters (Djurič et al., 1971; Kabata-Pendias and Pendias, 1979; Matthews and Thornton, 1982).

The metal contents found in plants in this study are much higher than those found in rural areas. In the case of lead, the reference value is no more than a few milligrams per kilogram dry weight of plant tissue and is often $\sim 1 \text{ mg kg}^{-1}$. The cadmium content is usually $< 0.5 \text{ mg kg}^{-1}$ dry weight of plant tissue.

In Poland, the tolerable concentration for vegetables is 0.3 mg kg^{-1} (fresh weight) for lead and 0.03 mg kg^{-1} (fresh weight) for cadmium (Monitor Polski, 1985). Lead concentrations were found which were 27 times this limit (Table 3). Of the total of 756 vegetable samples, only 170 did not exceed the lead standard. In the case of cadmium, concentrations were found that were 88 times the standard and only 17 samples were able to meet the standard (Table 4). The highest metal concentrations were recorded in vegetable leaves. The average excess relative to the standard for both metals was also calculated for the

TABLE 4

Cadmium concentrations in vegetables relative to the standard

Vegetables		Relative amount ^a		Number of samples not exceeding the standard
		Maximum	Mean	
Parsley	leaves	40	5	2
	roots	15	3	
Celery	leaves	88	13	1
	roots	49	10	1
Carrot	roots	22	4.5	4
Red beet	roots	17	4	9

^aObserved concentration divided by the standard concentration.
Number of samples, 756.

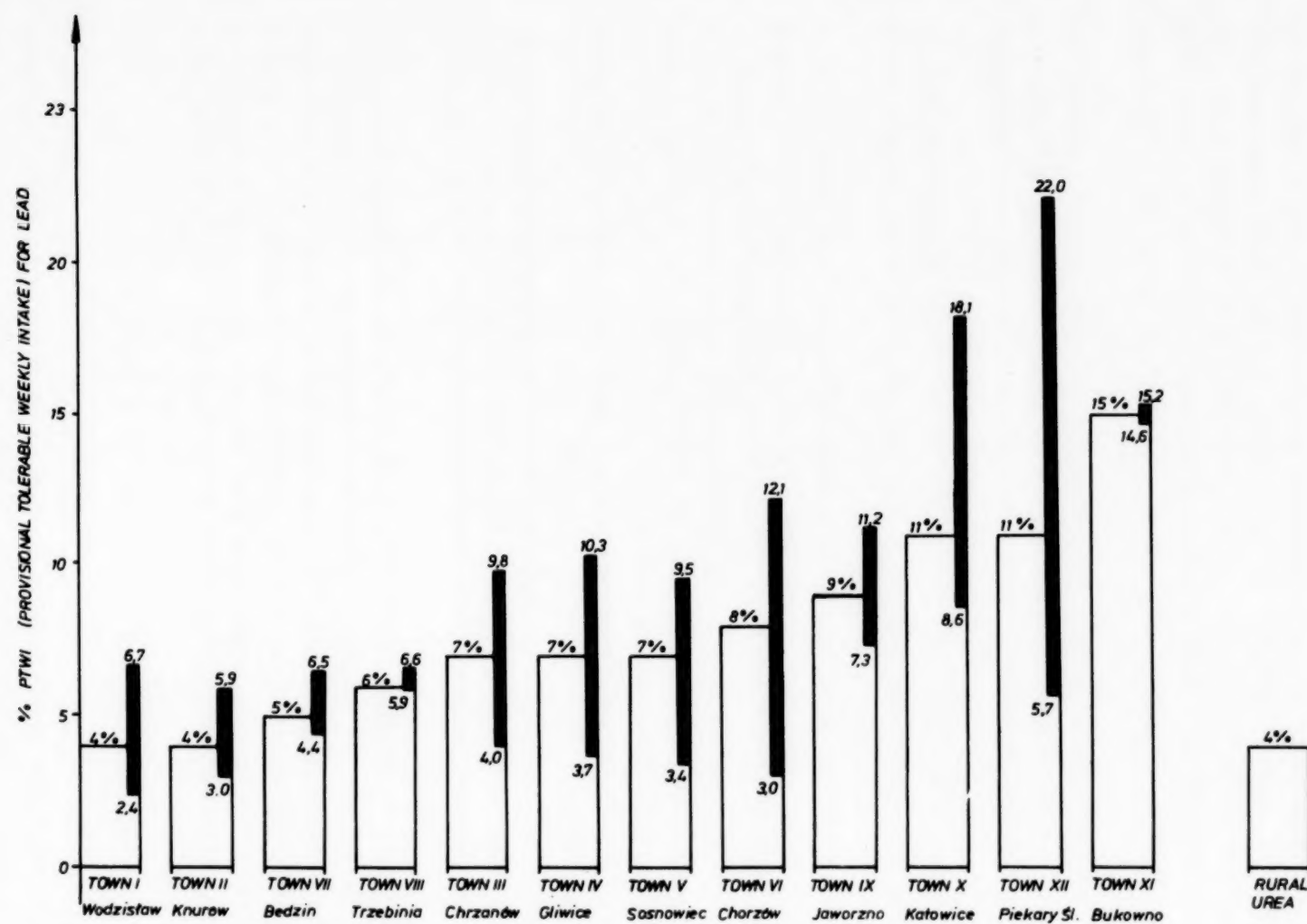


Fig. 2. Lead intake from vegetables cultivated in the Upper Silesia Region and rural areas.

vegetable samples from each town (Fig. 1). The highest metal concentrations were observed in the towns of Piekary, Bukowno and Katowice. The highest metal concentrations in atmospheric dust particles were also observed in these towns (Biuletyn WSSE, 1985).

When comparing soil and air concentrations with values found in vegetables contaminated with metals, higher accumulation levels were observed for cadmium than for lead. The lower lead levels could be attributed to two possible causes, soil pH or a high content of organic matter in the soils. The latter has been shown to be very important for lead (Harmsen, 1977; Doelman and Haanstra, 1979).

An attempt was also made to calculate exposure of consumers to metals. On the basis of our own questionnaire, data were collected concerning vegetable consumption by 205 families (Gzyl, 1986). The calculated results were expressed in percent of provisional tolerably weekly intake (PTWI).

According to the WHO/FAO, the amount of metals from all sources, should not exceed 3 mg and 0.4–0.5 mg per week for lead and cadmium, respectively (WHO, 1977, 1979).

In the reference areas, lead intake from vegetables did not exceed 4% of PTWI (Fig. 2), but vegetables from the surveyed allotments contributed between 2 and 22% of PTWI for lead. The corresponding cadmium intake in agricultural areas did not exceed 5% of PTWI, while vegetables from polluted areas contributed between 4 and 81% of PTWI, with the highest values recorded in Piekary, Bukowno and Katowice.

Figures 2 and 3 present minimum, maximum and mean lead and cadmium intake from vegetables.

It can be concluded that red beet and carrots are the major sources of metals supplied to humans, even though the highest concentrations were found in celery leaves and parsley. This resulted from the dietary pattern in the research area.

Preliminary random studies of vegetables from wholesale shops delivering vegetables to groceries in Katowice province confirm relatively low metal concentrations in these vegetables. The vegetables were supplied from neighbouring provinces. Elimination of carrots and red beet cultivated in polluted areas and replacing them with vegetables from other regions would reduce the metal intake to between 3 and 10% of PTWI for lead and between 7 and 50% of PTWI for cadmium.

CONCLUSIONS

The lead and cadmium content of soils and vegetables from 126 allotments in 12 towns of Katowice District exceeded both the quantities found in agricultural regions and the maximum allowable concentrations.

Lead intake from the analyzed vegetables contributes between 2 and 22% of the PTWI, calculated from all sources of exposure. The corresponding value for cadmium is from 4 to 81% of the PTWI.

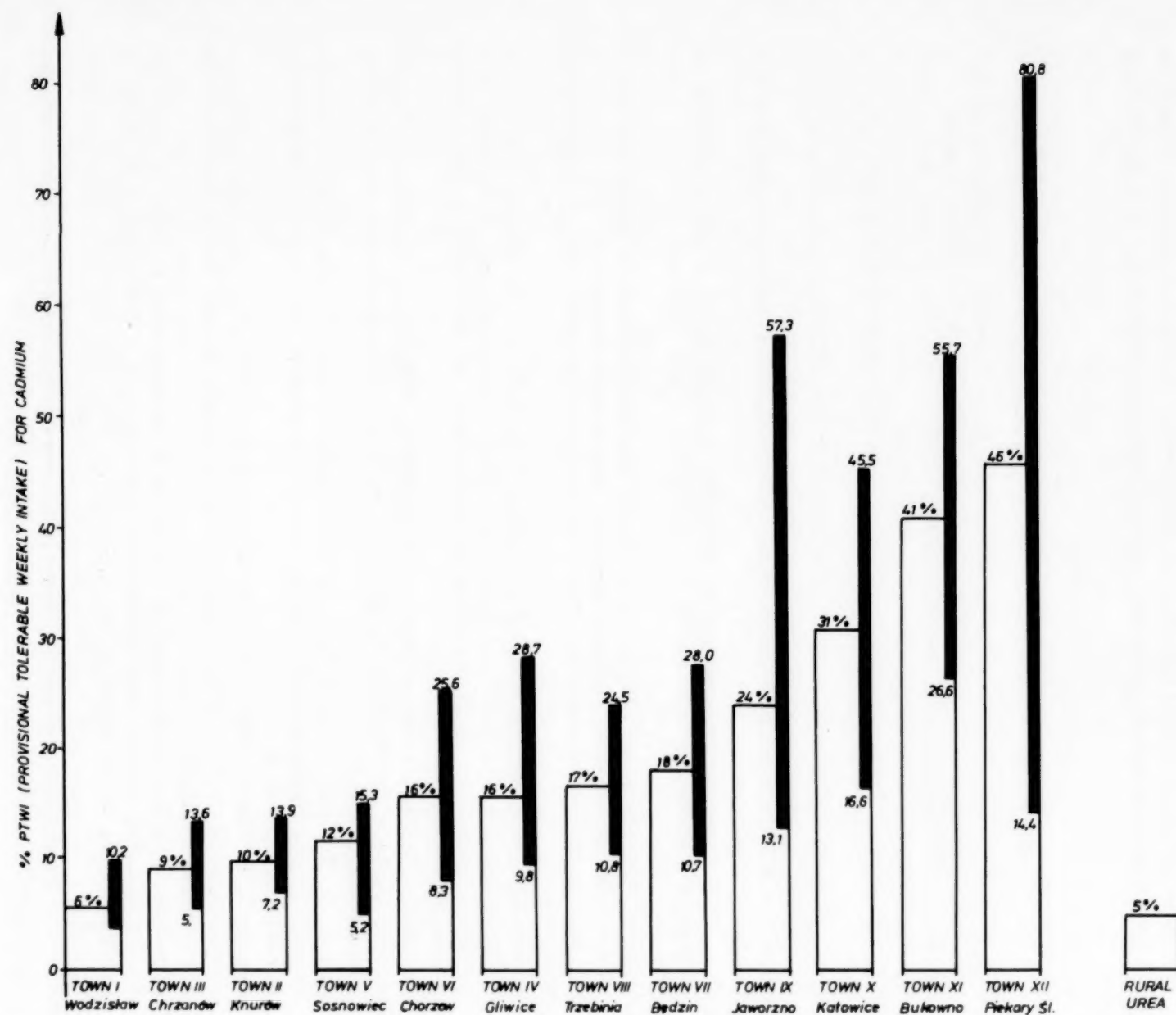


Fig. 3. Cadmium intake from vegetables cultivated in the Upper Silesia Region and rural areas.

A comparison of exposure to metals for consumers in Katowice District with consumers in other parts of Poland shows that the quantities in the more polluted area are from 2 to 5 times higher for lead and 2 to 16 times higher for cadmium.

The risk to consumers may be reduced by replacing some vegetables, particularly carrots and red beet, cultivated in Upper Silesia, by vegetables cultivated in non-polluted areas. This would result in a reduction of metal exposure from vegetables to between 3 and 10% of the PTWI for lead and between 7 and 50% of the PTWI for cadmium.

The differences in metal accumulation between vegetable species should be taken into account when planning agricultural management of a particular area.

REFERENCES

- Archer, F.C., 1980. Trace elements in soil in England and Wales. Inorganic pollution and agriculture. U.K. Ministry of Agriculture, Fisheries and Food. Ref. Book 326. HMSO, London.
- Benett, B.G., 1981. Exposure commitment assessment of environmental pollutants. No 1. MARC. Chelsea College, University of London; Vol. 1, pp. 27-29.
- Biuletyn WSSE, 1985. Zanieczyszczenie atmosfery w województwie katowickim. WSSE, Katowice, 1985.
- Djurič, D., Z. Kerin, L. Graovac-Leposavic, L. Novak and M. Kop, 1971. Environmental contamination by lead from a mine and smelter. Arch. Environ. Health, 23: 275-279.
- Doelman, P. and L. Haanstra, 1979: Effects of lead on the composition of organic matter. Soil Biol. Biochem., 11(5): 481-485.
- Gzyl, J., 1986. Narazenie konsumentów na toksyczne działanie ołowiu i kadmu zawartego w warzywach uprawianych w województwie katowickim. Praca doktorska. Katowice (unpublished).
- Harmsen, K., 1977. Behaviour of heavy metal in soils. Agricultural Research Reports 866. Centre for Agricultural Publishing and Documentation, Wageningen, Holland.
- Kabata-Pendias, A. and H. Pendias, 1979. Pierwiastki śladowe w środowisku biologicznym. PWRiL, Warszawa.
- Kucharski, R., E. Marchwińska, J. Gzyl, B. Karpińska, W. Lewandowski, K. Blaszk, Z. Nowińska, R. Janikowski, L. Molenda and U. Zielonka, 1982. Możliwości upraw warzyw w Pracowniczych Ogrodach Działkowych na terenie miasta Katowice. Ekspertyza NOT/SITR, Katowice (unpublished).
- Kucharski, R., E. Marchwińska, J. Gzyl and B. Karpińska, 1983. Ocena przydatności Pracowniczych Ogródów Działkowych do produkcji warzyw i owoców. Ekspertyza NOT/SITR, Katowice (unpublished).
- Kucharski, R., E. Marchwińska, J. Gzyl and B. Karpińska, 1984 a. Ocena przydatności Pracowniczych Ogródów Działkowych do produkcji warzyw i owoców. Etap II. Ekspertyza NOT/SITR, Katowice (unpublished).
- Kucharski, R., E. Marchwińska, J. Gzyl and B. Karpińska, 1984 b. Ocena przydatności Pracowniczych Ogródów Działkowych do produkcji warzyw i owoców. Etap III. Ekspertyza NOT/SITR, Katowice (unpublished).
- Marchwińska, E., R. Kucharski, J. Gzyl, B. Karpińska, W. Lewandowski, K. Skiba, Z. Nowińska, W. Jarosz and Z. Piesak, 1983. Możliwości upraw warzyw w Pracowniczych Ogrodach Działkowych na terenie województwa katowickiego. Biblioteka IOS-COS, Katowice (unpublished).
- Matthews, H.J. and A.K. Thornton, 1982. Seasons and species variation in the content of cadmium and associated metals in pasture at Shipham. Plant Soil, 60: 191-193.

- Monitor Polski 39, 1985. Zarządzenie Ministra Zdrowia i Opieki Społecznej.
- Monitor Polski 23, 1986. Zarządzenie Ministra Ochrony Środowiska i Zasobów Naturalnych.
- WHO, 1977. Environmental Health Criteria 3. Lead. World Health Organization, Geneva.
- WHO, 1979. Environmental Health Criteria for Cadmium. Interim Report. World Health Organization, Geneva.



Types of contributions	<p><i>Full papers</i> reporting original work.</p> <p><i>Short Communications.</i> A means for communicating urgent matter or the reporting of preliminary findings with a minimum of publication delay.</p> <p><i>Technical Notes.</i> Very brief descriptions of new, or modifications of existing, techniques which mark major advances and are of practical value.</p> <p><i>Letters to the Editor.</i> A means of allowing written discussion of papers published in the journal. Letters are accepted on the basis of originality and timeliness.</p> <p><i>Reviews.</i> Critical evaluation of existing data for defined fields of investigation together with considerations of historical development of topics. Those wishing to prepare a review should first consult the Managing Editor or Associate Editors concerning acceptability of topic and length.</p> <p><i>Proceedings</i> of symposia and/or conferences will be considered for publication. One of the editors should be contacted as early as possible to discuss details.</p>
Submission of papers	<p>The original and two copies of the manuscript may be submitted to one of the following addresses:</p> <p>Dr. E. I. Hamilton, Phoenix Research Laboratory, "Pengelebe", Dunterton, Milton Abbott, Tavistock, Devon PL19 0QJ, United Kingdom.</p> <p>Dr. J. O. Nriagu, National Water Research Institute, Box 5050, Burlington, Ontario L7R 4AG, Canada.</p> <p>They may also be sent to the nearest member of the Editorial Board.</p>
Manuscripts	<p>English is the preferred language although occasional contributions written in French or German will also be considered. Manuscripts should be typed in double spacing on consecutively numbered sheets of A4 size white paper allowing wide margins of at least 3 cm on both sides as well as top and bottom. The title of the paper should be concise and informative. It should be followed by the author's full name, academic or professional affiliations and addresses. An abstract, not exceeding 200 words, should then follow. It should identify the main points of the paper, not be a repetition of the title and, as far as possible, replace rather than supplement a "concluding" summary. The text should be divided into well-defined sections, each headed by a caption, e.g., Abstract, Introduction, Experimental, Results, Discussion, Acknowledgements, References.</p> <p>Avoid (or define, at first use) any non-standard abbreviations, unfamiliar terms, symbols and acronyms. Papers written in French or German should be accompanied by an English translation of all key words.</p>
Tables	<p>Tables should be typed in double spacing on separate pages and numbered in arabic numerals according to their sequence in the text. Each table should have a brief descriptive heading which makes its general meaning understandable without reference to the text.</p>
Illustrations	<p>The figures should be submitted in a form suitable for reproduction, drawn in Indian ink on drawing or tracing paper with lettering. They should preferably be of such a size that the same degree of reduction can be applied to all of them, and particular care should be taken to make any lettering sufficiently thick and large. Photographs should have good contrast and intensity. Sharp, glossy photographs are required to obtain good halftones. Photographs should be supplied in their final size. Draw bar scales on all micrographs instead of providing a numerical scale in the figure caption. Each illustration should be numbered according to the sequence of its appearance in the text, where they should be referred to as Fig. 1, Fig. 2, etc. Each illustration should have a legend, all the legends being gathered together on a separate sheet.</p>
Units, abbreviations, footnotes	<p>Authors are recommended to use SI units. If non-SI units are used, a conversion factor to SI units should be provided. Authors should follow the recommendations of the IUPAC Manual of Symbols and Terminology for Physico-Chemical Quantities and Units, <i>Pure and Applied Chemistry</i>, 21 (1970) 1, and its appendices. The IUPAC conventions should be used whether or not the paper is in English. Widely accepted forms of abbreviations should be used. The full expression followed by the abbreviation should be given the first time it appears in the text. Footnotes should only be used if absolutely essential. They must be indicated by asterisks. They should not be numbered and included with the references.</p>
References	<p>As the scope of the journal will cover a wide range of interests, two methods of reference quotation will be accepted. Manuscripts should contain one method throughout.</p> <p>Method (a): References in the text start with the name(s) of the author(s) followed by the publication date in brackets, e.g., Jones (1960) has shown the importance of . . . or, . . . has been described (Jones, 1960; Brown, 1961) . . . ; using chronological order. The reference list is in alphabetical order and typed (double-spaced) on sheets separate from the text. Journal names should be abbreviated as in <i>World Medical Periodicals</i> (3rd edition) published by the World Medical Association, New York. The full title of the paper should be given.</p> <p>Example: Oremland, R. S. and B. E. Taylor, 1978. Sulfate reduction and methanogenesis in marine sediments. <i>Geochim. Cosmochim. Acta</i>, 42: 209-214.</p> <p>Method (b): References are numbered in the order in which they are cited in the text and listed in numerical sequence on a separate sheet at the end of the article. The number, between brackets, should appear in the text at the appropriate places. In the reference list, periodicals [1], books [2] and multi-author books [3] should be cited in accordance with the following examples:</p> <ol style="list-style-type: none"> 1 H. Bartsch and R. Montesano, Mutagenic and carcinogenic effects of vinyl chloride. <i>Mutat. Res.</i>, 32 (1975) 93-114. 2 R. D. O'Brien, Toxic Phosphorus Esters: Chemistry, Metabolism and Biological Effects, Academic Press, New York, 1960, p. 74. 3 R. D. Marshall and A. Beuberger, in A. Gottschalk (Ed.), Glycoproteins, Vol. 5, Part A, Elsevier, Amsterdam, 2nd edn., 1972, Ch. 3, p. 251. <p>Abbreviations for the titles of journals should follow the system used by Chemical Abstracts.</p>
Reprints	<p>Fifty reprints of Regular Papers, Short Communications and Notes will be supplied free of charge. Additional reprints can be ordered by the authors. An order form containing price quotations will be sent to the author together with the proofs of the article.</p>

THE SCIENCE OF THE TOTAL ENVIRONMENT

Vol. 96 Nos 1 + 2

Contents

July 1990

(Abstracted/Indexed in: Biol. Abstr., Chem. Abstr., Curr. Contents AB & ES, Environ. Period. Bibliogr., Excerpta Med., Focus On: Global Change, Geo Abstr., Oceanogr. Lit. Rev., PASCAL/CNRS, Selected Water Resour. Abstr.)

Special Issue: Pathways of Man-made SO₂, NO_x and Metals in the Environment

<i>Preface</i>	ix
Chemical threat to the environment in Poland	
L. Pawlowski (Lublin, Poland)	1
Acid precipitation monitoring and research. Review of current Norwegian activities	
G. Taugbøl (Oslo, Norway)	23
Acidification in Norway — loss of fish populations and The 1000-Lake Survey 1986	
B.O. Rosseland and A. Henriksen (Oslo, Norway)	45
Acid precipitation: Biological monitoring of streams and lakes	
A. Fjellheim and G.G. Raddum (Bergen, Norway)	57
Concentrations of atmospheric SO ₂ , NO ₂ and dust in the Lublin coal basin area	
Z. Kozak, A. Figurski, J. Niećko, D. Kozak and R. Gierżatowicz (Lublin, Poland)	67
Calculations of long-range transported sulphur and nitrogen over Europe	
T. Iversen (Oslo, Norway)	87
The role of nitrogen oxides in the long-range transport of photochemical oxidants (Abstract only)	
Ø. Hov (Lillestrøm, Norway)	101
Metal solubility and pathways in acidified forest ecosystems of South Sweden	
D. Berggren, B. Bergkvist, U. Falkengren-Grerup, L. Folkeson and G. Tyler (Lund, Sweden)	103
Occurrence of heavy metals in water, phytoplankton and zooplankton of a mesotrophic lake in eastern Poland	
S. Radwan, W. Kowalik and C. Kowalczyk (Lublin, Poland)	115
Accumulation of heavy metals in a lake ecosystem	
S. Radwan, W. Kowalik and R. Kornijów (Lublin, Poland)	121
Total and extractable heavy metal content of some soils of the Lublin Coal Mining Region	
T. Filipek and L. Pawlowski (Lublin, Poland)	131
Assessment of aluminium mobilization and pathways in the Birkenes catchment, southern Norway	
R. Vogt, H.M. Seip, N. Christophersen and S. Andersen (Oslo, Norway)	139
Are mathematical models useful for understanding water acidification?	
A. Stone and H.M. Seip (Oslo, Norway)	159
Aluminium mobilization in soil and stream waters at three Norwegian catchments with different acid deposition and site characteristics	
N. Christophersen (Oslo, Norway), C. Neal (Wallingford, U.K.), R. Vogt (Nesoya, Norway), J.M. Esser (Ås, Norway) and S. Andersen (Oslo, Norway)	175
Effect of nitrogen on drought resistance of Norway spruce and Scots pine	
P. Nilsen (Ås, Norway)	189
Lead and cadmium contamination of soil and vegetables in the Upper Silesia region of Poland	
J. Gzyl (Katowice, Poland)	199

© 1990, ELSEVIER SCIENCE PUBLISHERS B.V.

0048-9697/90/\$03.50

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior written permission of the publisher, Elsevier Science Publishers B.V., P.O. Box 330, 1000 AH Amsterdam, The Netherlands.

Upon acceptance of an article by the journal, the author(s) will be asked to transfer copyright of the article to the publisher. The transfer will ensure the widest possible dissemination of information.

Submission of an article for publication entails the author(s) irrevocable and exclusive authorization of the publisher to collect any sums or considerations for copying or reproduction payable by third parties (as mentioned in article 17 paragraph 2 of the Dutch Copyright Act of 1912 and in the Royal Decree of June 20, 1974 (S. 351) pursuant to article 16b of the Dutch Copyright Act of 1912) and/or to act in or out of Court in connection therewith.

Special regulations for readers in the U.S.A. — This journal has been registered with the Copyright Clearance Center, Inc. Consent is given for copying of articles for personal or internal use, or for the personal use of specific clients. This consent is given on the condition that the copier pay through the Center the per-copy fee for copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Law. The per-copy fee is stated in the code-line at the bottom of the first page of each article. The appropriate fee, together with a copy of the first page of the article, should be forwarded to the Copyright Clearance Center, Inc., 27 Congress Street, Salem, MA 01970, U.S.A. If no code-line appears, broad consent to copy has not been given and permission to copy must be obtained directly from the author(s). All articles published prior to 1980 may be copied for a per-copy fee of US\$2.25, also payable through the Center. This consent does not extend to other kinds of copying, such as for general distribution, resale, advertising and promotion purposes, or for creating new collective works. Special written permission must be obtained from the publisher for such copying.

No responsibility is assumed by the Publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the materials herein. Because of rapid advances in the medical sciences, the Publisher recommends that independent verification of diagnoses and drug dosages should be made.

Although all advertising material is expected to conform to ethical (medical) standards, inclusion in this publication does not constitute a guarantee or endorsement of the quality or value of such product or of the claims made of it by its manufacturer.

This issue is printed on acid-free paper.

PRINTED IN THE NETHERLANDS

